METHODS FOR SULFATE AIR QUALITY MANAGEMENT

Volume 2

Main Text

by

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A6-061-87

EQL Report No. 16-2

First Printing December, 1977
Second Printing May, 1980

Environmental Quality Laboratory
California Institute of Technology
Pasadena, California 91125

Final Report to the

STATE OF CALIFORNIA
AIR RESOURCES BOARD

in

completion of research under
ARB Contract No. A6-061-87

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to Jeanie

ACKNOWLEDGMENTS

In early 1973, discussions with Professor Lester Lees led us to conclude that a "clean fuel" shortage would develop in the Los Angeles area in the late 1970's. Increased sulfur oxides emissions from increased fuel oil combustion were expected to eventually provoke a change in sulfur oxides emission control policy in Southern California. From Professor Sheldon Friedlander's instruction in the dynamics of aerosol formation, it was concluded that the sulfate air quality impact of these increasing sulfur oxides emissions would provide the most pressing questions for scientific research and for emission control strategy engineering. Professor Norman H. Brooks provided advice and encouragement throughout this project, and was indispensable in arranging for the substantial financial resources needed to complete this research. Professor Roger Noll's insight into the economics of regulation helped to frame questions for emission control strategy analysis. Professor Joel Franklin's instruction in stochastic processes led me to attempt the approach to air quality modeling employed in Chapter 3 of this study, while discussion with Professor Fredrick Shair helped to sharpen the physical assumptions built into that modeling effort. These faculty members have served as the advisory committee for this project. I am especially grateful to my principal advisor, Lester Lees, for giving me the liberty to pursue this research task by the methods which I felt would be necessary in order to cope with a complex air quality

problem over a period of many years within the context of one of the world's most extensively industrialized urban areas.

Without the advice on computing provided by Dr. Robert C. Y. Koh, completion of this research project within a reasonable length of time would have been impossible. Nearly all of the computations performed in this study were expedited by use of Bob Koh's universal data handling system called MAGIC. The computer-generated graphs in this thesis are examples of the excellent results which were quickly attainable by use of MAGIC.

Many members of the staff of Caltech's Environmental Quality Laboratory contributed to this project's success. The energy and sulfur balance study of Appendix A3 was co-authored by Pamela S. McMurry, while the crude oil characterization of Appendix A1 was co-authored by James Houseworth. David Sarokin edited the graphics. Anna Pechanec persisted through three consecutive attempts to reproduce previously published traffic count data for Los Angeles until we got the emissions inventory grid aligned properly. Gregory J. McRae read and commented on drafts of this work, and (believe it or not) succeeded in shortening the final version by several hundred pages. Charles Hales, Betsy Krieg, Tom Lawler and Lewis Hashimoto helped me to acquire the raw data for this study, almost all of which had to be transcribed by hand onto computer load sheets, followed by keypunching. They also helped with literature searches and preliminary data analysis tasks.

Margo Huffman, Pat Hofmann, Diane Davis, Jeanie Cass and Dana Leimbach typed this manuscript. Pat Rankin organized the flow of work during the typing phase. Jeanie Cass prepared the index to contents, figures and tables. Their patience with many revisions is gratefully acknowledged.

Work in this study has benefited from discussions with technical staff of the Environmental Quality Laboratory, Dr. John Seinfeld's research group in Chemical Engineering, and Dr. Sheldon Friedlander's group in Environmental Health Engineering. In particular, thanks are due to Dr. Robert G. Lamb, who took the time to comment on the air quality model derived in Chapter 3. While not all of the improvements that he suggested could be incorporated within our computing budget, the model validation effort of Chapter 5 benefited greatly from a few last-minute changes, particularly from his challenge that horizontal diffusion could not be neglected. Conversations with Drs. Paul T. Roberts, Warren H. White, Susanne Hering, Cliff Davidson, Peter H. McMurry, William Goodin and John Trijonis have been useful in hammering out approaches to specific problems as they arose in the course of this work.

The South Coast Air Quality Management District (and its predecessor agencies) went to considerable effort to cooperate in providing data for this study. Special thanks are due to Eric Lemke, Janet Dickinson, John Nevitt, Arthur Davidson, Margaret Brunelle,

Margil Wadley, Wayne Zwiacher, Ken Overturf, Julian Foon, Paul Chu, Sanford Weiss, Robert Murray, Herbert Whitehead, Martin Kaye, and Steve Menkus for answering an endless number of questions or for making staff available to provide answers when information was needed that went beyond that normally required to complete the District's mission. Joseph Stuart and Robert Lunche directed the District during the period that this work was performed.[1]

Staff of the Southern California Edison Company, Chevron Research Corporation, Union Oil Company, the Southern California Gas Company, Kaiser Steel, and KVB Incorporated have cooperated by providing data for this analysis, or by commenting on work in progeess. The librarians at Union Oil and at ARCO have been helpful in obtaining documents not normally collected by a university library.

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[1]During the period of the research project, the Los Angeles Air Pollution Control District, the Orange County Air Pollution Control District, the Riverside County Air Pollution Control District and the San Bernardino County Air Pollution Control District were first consolidated into the Southern California Air Pollution Control District and then reorganized into the South Coast Air Quality Management District. Throughout this thesis, the attempt has been made to cite the organizational name prevailing at the time that a particular piece of referenced information was collected. The abbreviation APCD when used refers to the work of the above organizations.

This work was carried out within the academic program of the Environmental Engineering Science Department of the California Institute of Technology. The Environmental Quality Laboratory at Caltech provided a financial foothold for the project and much staff assistance. The author's support was provided by the Joseph Warren Barker Fellowship in Engineering, given by the Research Corporation; by a Rockwell International Graduate Fellowship, and by Graduate Research Assistanships financed by research grants and by private gifts to the Environmental Quality Laboratory. The bulk of the cost of this project was met by a grant from the Ford Foundation (No. 740-0469) and by the California Air Resources Board (Contract No. A6-061-87).

The California Air Resources Board and their Research Department headed by Dr. John Holmes have cooperated by giving us free rein to approach this problem without constraint or preconditions. Jack Suder has been the contract monitor. All findings and conclusions are solely the responsibility of the authors and the Caltech advisory committee.

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ABSTRACT

Particulate sulfate air pollutants contribute to visibility deterioration and are of current public health concern. This study develops the technical understanding needed for sulfate air quality control strategy design. Methods which link sulfate air quality and air quality impacts on visibility to the cost of controlling sulfur oxides air pollutant emissions are presented. These techniques are tested by application to the Los Angeles Basin over the years 1972 through 1974.

An air quality simulation model is developed which directly calculates long-term average sulfate concentrations under unsteady meteorological conditions. Pollutant concentrations are estimated from Lagrangian marked-particle statistics based on the time sequence of historical measured wind speed, wind direction and inversion base height motion. First order chemical reactions and ground level pollutant dry deposition are incorporated within a computational scheme which conserves pollutant mass.

Techniques are demonstrated for performing both mass balance and energy balance calculations on flows of energy resources containing sulfur throughout the economy of an air quality control region. The energy and sulfur balance approach is used to check the consistency of a spatially and temporally resolved air quality modeling emission inventory for the South Coast Air Basin.

Next the air quality model is validated against sulfur oxides emissions and sulfate air quality patterns observed in the Los Angeles Basin over each month of the years 1972 through 1974. A seasonal variation in the rate of SO_2 oxidation to form sulfates is inferred. Overall average SO_2 oxidation rates of about 6% per hour prevail during late spring, summer and early fall, while mean SO_2 oxidation rates of between 0.5% per hour and 3% per hour prevail from October through February of our test years. From the model results, it is concluded that three to five major SO_x source classes plus background sulfates must be considered simultaneously at most monitoring sites in order to come close to explaining observed sulfate levels. The implication is that a mixed strategy aimed simultaneously at a number of specified source types will be needed if substantial sulfate air quality improvements are to be achieved within this particular airshed.

Techniques are developed for analysis of the *long-run* impact of pollutant concentrations on visibility. Existing statistical models for light scattering by aerosols which use particle chemical composition as a key to particle size and solubility are modified so that the relative humidity dependence of light-scattering by hygroscopic aerosols could be represented in a more physically realistic manner. Coefficients are fitted to the model based on ten years of air pollution control agency routine air monitoring data taken at downtown Los Angeles. Sulfates are found to be the most effective light scatterers in the Los Angeles atmosphere. It is estimated that the

visibility impact of reducing sulfates to a half or to a quarter of their measured historic values on each past day of record would be manifested most clearly in a reduction in the number of days per year of less than three-mile visibility. The number of days of average visibility less than ten miles would be little affected.

Two retrospective examples are worked to show how the results of the air quality simulation models may be used to define a variety of sulfate air quality control strategy options. It is suggested that a package of technological emissions control measures and institutional changes (including natural gas price deregulation) may provide greater improvements in both sulfate air quality and visibility at less cost than can be obtained from a purely technological solution to the Los Angeles sulfate problem.

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CHAPTER 1

INTRODUCTION

1.1 Objective

The objective of this research is to create a policy-responsive mathematical description of an urban sulfate air pollution problem. The study is placed in the context of the Los Angeles Basin, but methods of analysis are developed which have general application to air pollution control strategy design.

The nature and origin of sulfate pollution in an urban airshed first will be described. Existing air quality and meteorological data bases will be assembled into an organized picture of the pollution problem at hand. Sulfur balance and energy balance techniques will be developed which tie sulfur oxides air pollutant emissions to their origin in a regional energy economy. Then mathematical models will be derived and tested which simulate emissions/air quality relationships, and air quality impacts on local visibility. A technical foundation thus will be laid for future studies of the impact of alternative emissions control strategies on sulfate air quality.

1.2 The Importance of Understanding Sulfate Air Quality Management Options

Control of sulfur oxides air pollutant levels is one of the most persistent air quality problems facing industrialized societies. On a global basis, combustion and processing of sulfur-bearing fossil

fuels and smelting of sulfur-bearing ores leads to the release of 65×10^6 metric tons of sulfur into the atmosphere yearly (Friend, 1973). While naturally occurring sulfur sources exceed this man-made pollution burden on a global-average basis, the fuel-burning origin of man's sulfur oxides emissions often means that pollutants are generated in close proximity to population centers. When an urban atmosphere becomes overloaded with sulfur oxides and particulate matter, well publicized public health disasters occasionally have occurred: the Meuse Valley, Belgium (1930); Donora, Pennsylvania (1948), and London, England (1952). Other far less dramatic consequences of sulfur oxides pollution are present on a more or less continuous basis in many urban areas, as will be discussed shortly.

Most of man's sulfur oxides emissions to the atmosphere are in the form of sulfur dioxide gas. Sulfur dioxide is known to be a mild respiratory irritant at elevated concentrations and is capable of inflicting damage to vegetation (National Research Council, 1975). Because of the predominance of SO_2 as the primary pollutant being emitted, and perhaps because it has been readily measurable for many years, current National Ambient Air Quality Standards for sulfur oxides in the United States (and the standards of most other nations) are stated solely in terms of limits on sulfur dioxide concentrations. As a result of this attention, extensive progress has been made in designing emissions control strategies aimed at achieving legally mandated limits on SO_2 concentrations.

In accordance with the requirements of the Clean Air Act (42 U.S.C.

§§ 1857 et seq.) in the United States, nearly every state has adopted an Implementation Plan containing a sulfur dioxide abatement strategy. Over the decade 1975 through 1985, it has been projected (Temple, Barker and Sloan, 1976) that the electric utility industry alone will incur capital expenditures of 11.6 billion dollars in order to comply with existing Federal SO_2 emission control policies. Sulfur dioxide abatement is thus one of the most expensive large scale environmental control programs undertaken in the United States. In view of the large fixed costs involved, it is important that sulfur oxides control strategies once adopted continue to serve long-run needs.

Unfortunately, control strategies aimed at reduction of sulfur dioxide levels alone may not address themselves to some of the most important consequences of burning sulfur-bearing fuels. Sulfur dioxide gas has been shown to undergo atmospheric oxidation to form suspended particulate sulfates.[1] These sulfate particles tend to accumulate in a size range around 0.5 microns in diameter (Hidy et al., 1975). Particles of this size are extremely effective scatterers of light (Middleton, 1952) and are also capable of deep penetration into the lung (Task Group on Lung Dynamics, 1966). In addition, there is a body of toxicological and epidemiological evidence suggesting that sulfate particulates are

---

[1] As used in this study, the definition of "sulfates" is an operational one: particulate sulfur oxides collected on glass fiber filters by high volume sampling and measured as $SO_4^=$ ion by wet chemical methods such as those described later in this study. The term "sulfates" thus denotes a broad class of particulate sulfur oxides in the atmosphere, including sulfuric acid mist, ammonium sulfate and bisulfate, and metallic sulfate salts, to name but a few of the more prominant components of this particulate complex.

much more irritating to the respiratory system per unit mass concentration than an equivalent amount of sulfur present as SO_2 alone (National Research Council, 1975). Sulfate air pollutants are thought to play an important role in the acidification of rain water (Committee on Mineral Resources and the Environment, 1975), and can be associated with chemical attack on materials and visibility deterioration (Middleton, et al., 1970).

Concern for these known or anticipated adverse effects of particulate sulfur oxides has prompted an extensive review of current knowledge in this area by the National Academy of Sciences (National Research Council, 1975). They note that air pollution control efforts during the past decade have generally led to a substantial reduction in urban sulfur dioxide concentrations. In contrast, suspended sulfates levels have remained largely unchanged in urban areas and may have increased in rural areas. *In short, apparently effective strategies currently employed for reducing SO_2 concentrations do not appear to lead to corresponding reductions in sulfate levels.*

If one were to accept that both ambient SO_2 and regionally enriched sulfate levels have a common source in man's sulfur oxides air pollutant emissions, a paradox would seem to arise from the failure to control both jointly. One fairly straightforward explanation for this situation, however, has been offered (National Research Council, 1975) as follows. In spite of the reduced SO_2 concentrations in urban areas, total sulfur oxides emissions from man's activities in the United States have been increasing at about 4 percent annually over the past decade.

Urban SO_2 reductions have been achieved by localized use of low sulfur fuels and by separating SO_2 emissions spatially from the immediate vicinity of population centers. Growth in fuel burning for electric power generation has been shifted to rural areas, and tall stacks have been used to inject pollutants higher into the atmosphere. Population exposures to sulfur dioxide associated with close proximity to a primary emission source thus have been reduced.

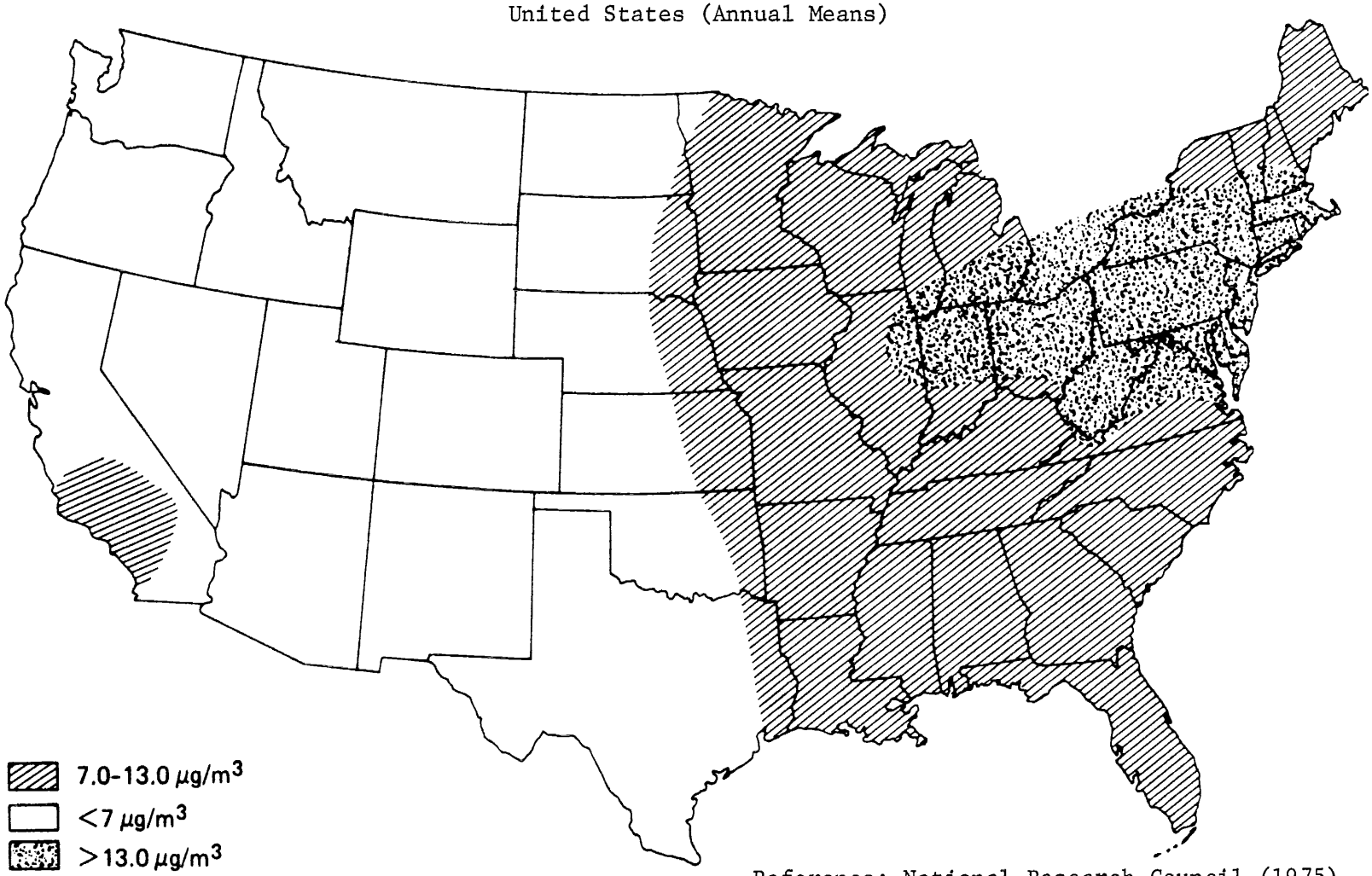
Man-made sulfates are largely a decay product of sulfur dioxide emissions. Sulfates are formed in the atmosphere over intermediate to long travel distances downwind from a sulfur dioxide emissions source. Widespread dispersion of pollutants would occur over long travel times regardless of steps taken to separate initial emissions from local receptor populations. Therefore the National Research Council study suggests that regional sulfates levels depend on total regional sulfur oxides emissions more than they depend on close proximity to a given emission source.

The widespread regional nature of sulfate air pollution problems is illustrated in Figure 1.1. Two areas of the United States are seen to be affected: the entire eastern United States, and the South Coast Air Basin of Southern California which contains metropolitan Los Angeles.

Large uncertainties presently frustrate formulation of sulfur oxides emissions control plans which <u>will</u> achieve control over sulfate levels. In a recent position paper, the U.S. Environmental Protection Agency (1975) stated that a National Ambient Air Quality Standard for

FIGURE 1.1

Geographical Distribution of Typical Urban Sulfate Levels in the United States (Annual Means)



Reference: National Research Council (1975).

particulate sulfates would not be proposed for at least three to five years due to a lack of clear understanding of several fundamental aspects of the sulfate pollution syndrome. More complete information is wanted to characterize atmospheric sulfate concentrations, health and welfare effects, chemical transformation/transport interactions, and emissions control options.

There is, in our opinion, a danger that if this additional information needed to formulate sulfate air quality control strategies is sought piecemeal, an improved decision-making capability may not result. Health and welfare effects research may be conducted in geographic regions for which emissions and air quality information are either lacking or poorly organized. Emissions control strategy design might be confined to regions with coal combustion problems that are not representative of the petroleum dominated fuel use in many of the nation's coastal population centers. Air quality models may be developed in the absence of an appreciation that they are needed to clarify a choice between long-run commitments of resources to possible emission control alternatives. Perhaps the most fundamental uncertainties in control strategy development lie in the dilemmas that will arise if small pieces of the problem analyzed separately fail to integrate into a comprehensive picture of control strategy costs and effects prior to the time when public pressure to make some costly choices becomes overwhelming.

For that reason, this research project will concentrate on developing the tools needed for sulfate air quality control strategy design

within the context of a single well chosen case study. Emphasis is placed wherever possible on development of techniques which utilize only that information commonly available from air pollution control agency historic data bases and other existing public records. This is done in recognition of the fact that a truly useful air quality control strategy design procedure must not only lead to economically efficient control strategy options; the design procedure itself must be economical or it will not be used. Expensive new field measurement programs needed to acquire specialized data bases are probably beyond the means of most state and local regulatory agencies.

The need for this approach to an improved understanding of sulfate air quality management options is apparent. In the words of the National Academy of Sciences Committee:

> Decisions to be made on sulfur oxide emissions from power plants will involve tens of billions of dollars in electrical generation costs in the next decade and massive effects on human health and welfare. Greatly expanded efforts should be made to develop improved models and data for use on a case by case basis to improve decisionmaking on emission control strategy alternatives. [National Research Council, 1975].

1.3 The Approach Used in This Work

An air pollution control strategy is a systematic means of restricting air pollutant emissions in order to achieve a desired level of ambient air quality or some limited measure of air pollution damage. Air pollution control strategy development is a design process in which the objective is to define a variety of possibly acceptable courses of action. Each alternative should be an efficient one, that is to say, a set of control possibilities which contains some desirable

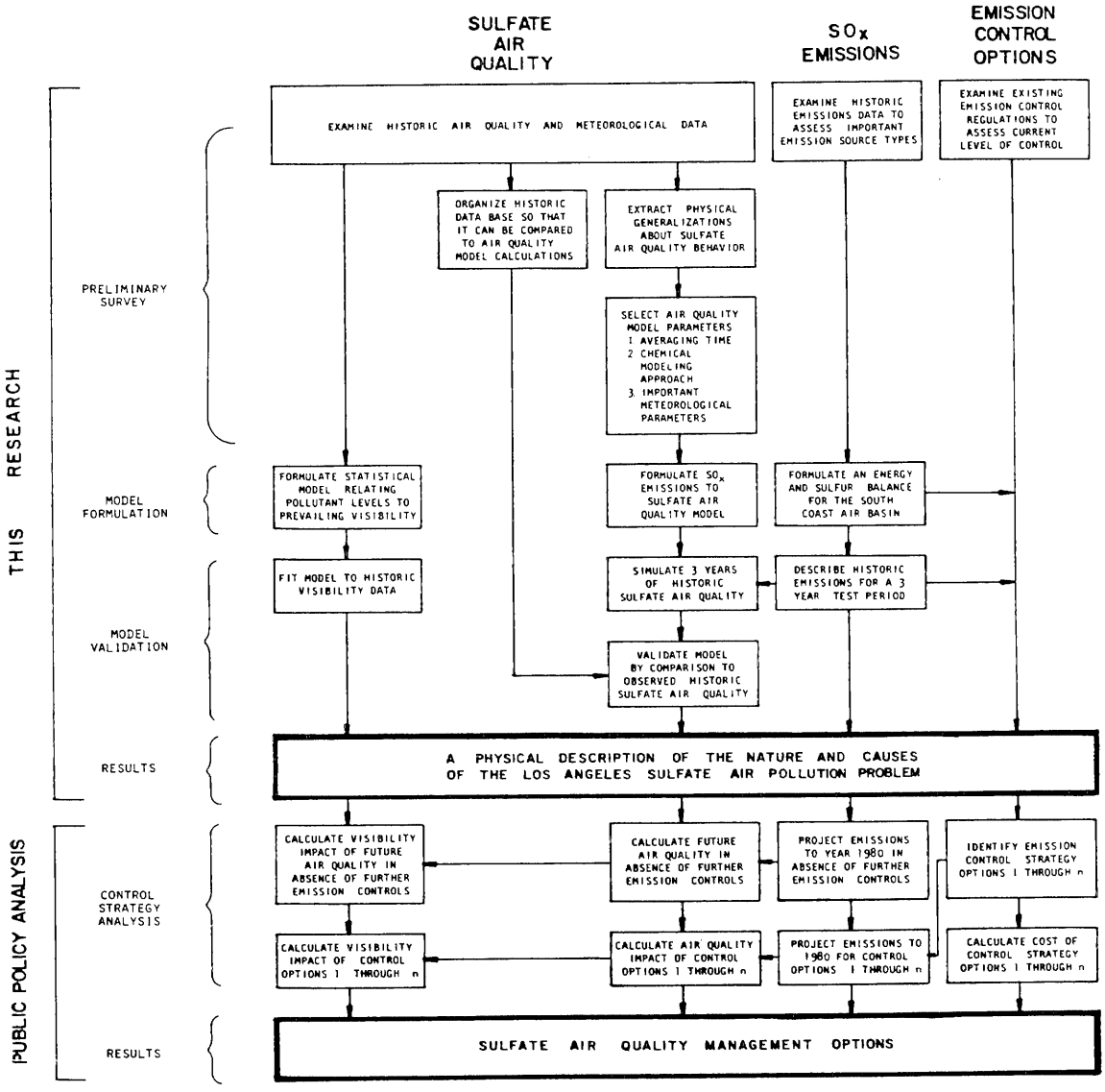
properties which cannot be attained at any lower economic cost. From among this large variety of possibly acceptable courses of action, decision-makers are free to choose with the knowledge that they are not wasting resources in order to attain the result selected.

Figure 1.2 outlines an approach to sulfate air quality control strategy design. That process naturally divides into two phases. A flexible physical description of the air pollution problem first is constructed, then alternative courses of action may be evaluated by perturbing the current emissions control strategy and observing the airshed's response.

The first of these tasks is chosen as the subject for this project. A policy-responsive mathematical description of an urban sulfate air pollution problem will be constructed. The most prominent features of that air quality problem first will be identified by analysis of historical air monitoring data. Sulfur oxides pollutant emissions next will be linked to their origin in regional energy use patterns. Then mathematical models will be developed which describe emissions/air quality relationships and air quality impacts on local visibility. It is important to note at the outset that these mathematical models themselves no more constitute an air pollution control strategy design procedure than having a hammer constitutes building a chair. Unless a prototype procedure is demonstrated for bringing these tools to bear on a real problem, the tools' existence is of very superficial importance. For that reason, the application of analytical tools to the Los Angeles sulfate problem will form the core around which this discourse is organized.

FIGURE 1.2

Research Plan



The first step in this air quality control strategy design procedure is to define the nature of the air quality problem at hand. From statistical analysis of existing air quality data one can draw important generalizations about the physical processes most directly influencing sulfate concentration changes. These physical assumptions will later be used to reduce the complexity of a deterministic emissions to air quality model to manageable proportions.

At the outset, only a huge mass of disorganized ambient air quality measurements will be available. An orderly picture of sulfate air quality behavior will be shown to exist. Spatial gradients in sulfate air quality are explored to verify an enrichment in atmospheric sulfate levels above natural background in the Los Angeles area. Day-to-day fluctuations in sulfate concentrations will be used to show that sulfate pollutant levels rise and fall in a closely coupled fashion over a large region of Southern California. The causes of these day-to-day concentration changes are explored in terms of specific meteorological and co-pollutant variations. Sulfate concentration changes are shown to depend on daily mixing depth in the Los Angeles Basin, and on factors such as relative humidity plus suspended particulate and oxidant concentrations which would be expected to affect the rate of oxidation of SO_2 to form sulfates. Then a selection is made of the important features of sulfate air quality behavior in Los Angeles which could be used to construct and validate a deterministic emissions to air quality simulation model.

Existing models relating emissions to long-term average air quality are reviewed and found to lack the ability to even approximately model several of the features most important to Los Angeles sulfate air quality such as air parcel retention time or strong temporal changes in emission source strength. A new type of long-run average air quality model for slowly reacting air pollutants is then developed based on long-run average Lagrangian marked particle statistics.

A spatially resolved inventory of sulfur oxides emissions is assembled for each month of three test years, 1972 through 1974. This inventory is actually constructed in the form of a fuel switching simulation model such that emissions may be projected to future years in which natural gas curtailment will have altered the spatial distribution of sulfur-bearing fuel oil combustion. The emissions generation model is linked to the air quality model, and predicted sulfate air quality for the test years 1972 through 1974 is compared to actual historical measurements.

One tangible benefit from lowered future sulfate levels would be an improvement in visibility in the Los Angeles Basin. A statistical model is formulated which explains the long-term distribution of prevailing visibilities at Los Angeles in terms of changes in pollutant levels and relative humidity. The model is tested against a decade of atmospheric observations at Los Angeles, then projections are made of the future distribution of visibilities which would be expected if sulfate concentrations in the Los Angeles Basin were significantly reduced.

1.4 Relationship of This Research to Future Work

The analytical techniques developed in this study are designed to be applied to a public policy analysis of sulfate control strategy options in the central portion of the South Coast Air Basin of California, as outlined in Figure 1.2. That emissions control strategy study could be pursued as follows.

Emissions projections for the early 1980's could be made on the basis of anticipated natural gas curtailment and electric generation levels in those years. The effect of sulfuric acid mist emissions from catalyst-equipped cars should be introduced into the model. Then air quality levels resulting from this 1980's emissions pattern could be projected using the previously validated air quality model.

An emissions control study then could be conducted to establish the cost of altering future sulfur oxides emissions levels. Specific options within three general classes of emissions control techniques should be explored: purchased naturally occurring low sulfur fuels, fuel desulfurization, and stack gas cleaning. Costs imposed on an acceptable emissions control program by institutional barriers, such as Federal Power Commission gas price regulation, should be discussed. Then the least-cost means of achieving a variety of altered future sulfate air quality patterns could be established.

An estimate could be made of the impact of each sulfate control strategy on visibility at downtown Los Angeles. Benefits to visibility could be arrayed against the air quality levels and the cost of each control strategy option. Decision-makers then would have a tool for

selecting an air quality control strategy from a set of options, each of which is an economically efficient means of attaining the air quality levels and distribution of control costs described.

1.5 Relationship of This Study to Previous Work and Ongoing Research

The only previous sulfate air quality control strategy study for a multiple source urban setting was conducted by Trijonis et al. (1975). The present study provides the foundation for improving upon such previous efforts by statistically exploring the underlying physical causes of sulfate air quality fluctuations in order to improve modeling capability, by developing a unique deterministic spatially resolved diffusion model to suit this application, by illustrating the importance of both mass balance and energy balance calculations when dealing with a sulfur oxides pollution problem, and by examining benefits to visibility from sulfate air quality control. Sulfate air quality control strategies in the comprehensive economic and technical sense used here have also been approached by the previously mentioned National Research Council (1975) committee, but only for hypothetical cases most directly related to siting of single coal-fired power plants in the eastern United States.

Other sulfate air quality modeling or control strategy studies are underway at the present time. The Sulfate Regional Experiment (SURE) project is proceeding under sponsorship by the Electric Power Research Institute. The Multi-State Atmospheric Power Production Pollution Study (MAP3S) is being conducted by the U.S. Energy Research and Development Administration. Both of these projects have as an objective the

identification of the contribution of the electric utility industry to sulfate levels observed in the Northeastern United States. The Midwest Interstate Sulfur Transformation and Transport (MISTT) project is being conducted by the U.S. Environmental Protection Agency to determine sulfate formation mechanisms in sufficient detail that they may be incorporated explicitly within air quality simulation models. Economic evaluation of sulfate air quality control strategies involving the electric utility industry is being pursued by the U.S. Environmental Protection Agency and Teknekron Inc. as part of the Integrated Technology Assessment of Electric Utility Energy Systems project. The Long Range Transport of Air Pollutants (LRTAP) study is being conducted by the Organization for Economic Cooperation and Development (OECD) to determine the relationship between sulfur oxides emissions and sulfate deposition in Western Europe.

1.6 An Introduction to Los Angeles Sulfur Oxides Air Pollution

When the smog problem in the Los Angeles Basin was first investigated, attention was focused on sulfur oxides emissions from industrial sources. Most of these emissions to the atmosphere were in the form of sulfur dioxide gas. Additional atmospheric measurements also identified particulate sulfur compounds, often referred to in the early literature as sulfuric acid mist or its gaseous precursor, sulfur trioxide. These particulate sulfur compounds were initially believed to be responsible for "thirty to sixty percent of the total reduction in visibility" at Los Angeles (Los Angeles Air Pollution Control District, 1950). It was also soon recognized that there was something unusual about Los Angeles sulfate air quality. The Los Angeles

atmosphere exhibited sulfate concentrations comparable to those of cities in the industrial northeastern United States despite the fact that sulfur dioxide emissions in Southern California were modest by comparison. At the conclusion of an extensive aerometric survey of the Los Angeles area (Renzetti, et al., 1955), the question was posed, "Why are the sulfate and nitrate concentrations in the particulate loading in smog higher in Los Angeles than in other cities?" Twenty years later that question is only partially answered.

As the sulfur dioxide emission control program succeeded in reducing ambient SO_2 concentrations, and as the extremely complex chemical nature of photochemical smog became better understood, public attention was directed at the control of emissions from the automobile which dominated other aspects of local air quality. Recently, two things have happened which suggest that current control strategies for sulfur oxides should be reviewed.

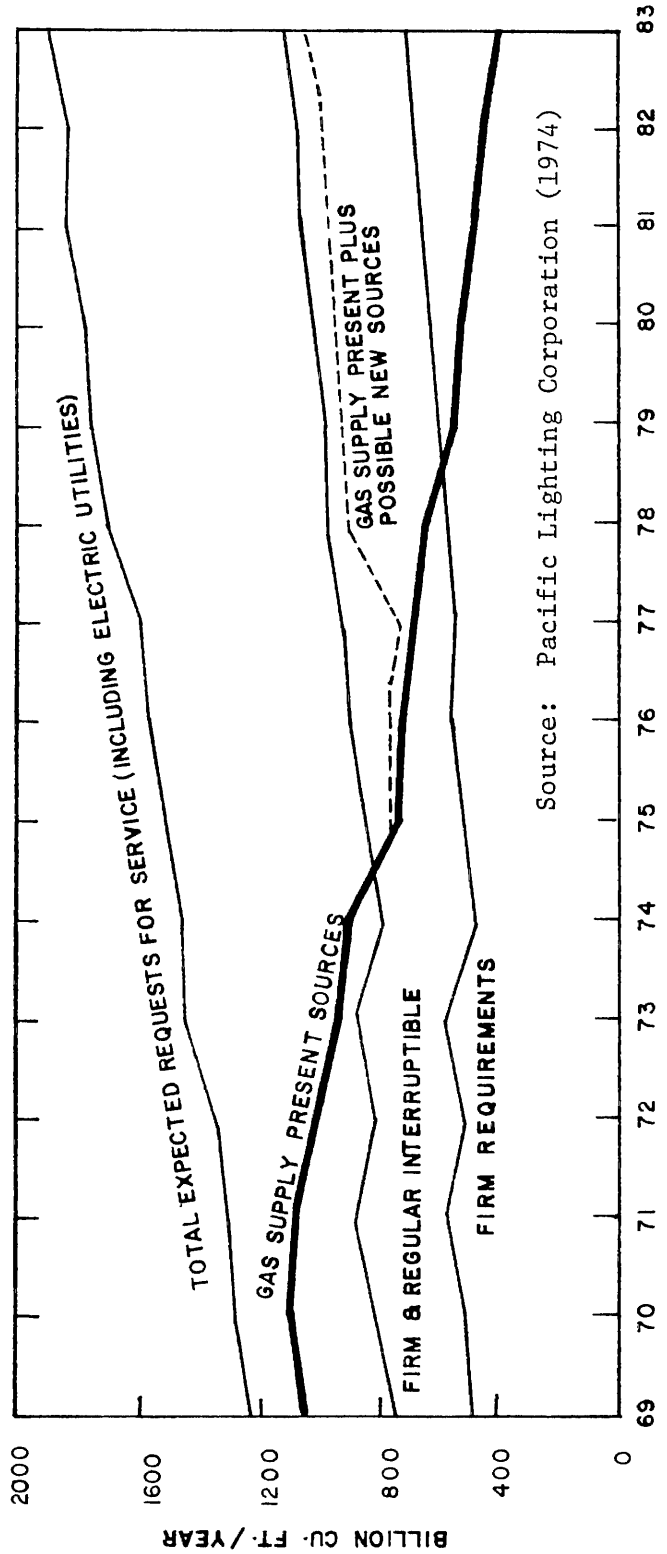
The first of these is a rekindling of scientific interest in the role of particulate sulfates in the Los Angeles atmosphere. In 1969 an academically organized study of aerosol behavior (Whitby et al., 1971; Hidy et al., 1972) noted that man's contribution to the aerosol loading in Los Angeles was concentrated in submicron particles which were easily respirable. Many of these submicron aerosols were found to be the result of gas to particle conversion processes occurring in the atmosphere. Sulfates were identified as a major fraction of this "secondary" particulate burden. A large-scale Aerosol Characterization Study sponsored by the California Air Resources Board followed

(Hidy, et al., 1975). This study concluded, as had early investigation in the 1950's, that sulfates were largely responsible for the well-known visibility deterioration at downtown Los Angeles. A concurrent study by Roberts (1975) examined Los Angeles sulfate air quality and measured the rate of conversion of SO_2 to form sulfates in the atmosphere. Translation of these findings into design of an improved sulfur oxides air pollution control strategy for Los Angeles remains to be accomplished.

A second compelling reason for focusing on Los Angeles is a potential increase in basin-wide sulfur dioxide emissions due to curtailment of natural gas deliveries to Southern California. Figure 1.3 shows the Pacific Lighting Corporation's (1974) estimated gas supplies from existing sources in contrast to projected requests for service at current prices. It had been estimated by the Los Angeles Air Pollution Control District (1975a) that substitution of sulfur-bearing fuel oil for natural gas combustion over the next few years could increase SO_2 emissions in Los Angeles County from a low of 257 tons per day in 1970 to a level of about 470 tons per day by 1979 in the absence of any further emission controls beyond those existing in 1974. On the same basis, the California Air Resources Board estimated that SO_2 emissions in the entire South Coast Air Basin (which contains Los Angeles County) could increase from a 1973 level of 515 tons per day to a level of between 720 and 920 tons per day by 1983 (California Air Resources Board, 1975). Control of the impact of this potential increase in sulfur oxides emissions is a matter of current public policy importance.

FIGURE 1.3

PACIFIC LIGHTING CORPORATION
NATURAL GAS SUPPLY VS. EXPECTED REQUESTS
FOR SERVICE AT CURRENT PRICES



Source: Pacific Lighting Corporation (1974)

Prompted by the impending emissions increase, the local findings concerning visibility, and the previously mentioned national debate over the health consequences of sulfate air quality, the California Air Resources Board recently adopted an air quality goal for total suspended particulate sulfates. A 24-hour average sulfate concentration of 25 micrograms per cubic meter is not to be exceeded.[2] Some initial steps also have been taken to blunt the expected SO_x emissions increase by decreasing the sulfur content of fuel burned in the Los Angeles Basin. As yet, no comprehensive emission control strategy has been adopted for meeting the state sulfate air quality goal in Los Angeles over the long term. If such actions are proposed, they undoubtedly will be quite expensive. Substantial savings might be achieved by better understanding the options available for managing sulfate air quality in this particular air basin in an economically efficient manner.

1.6.1 Sulfur Dioxide Emission Trends

A brief historical account (Los Angeles Air Pollution Control District, 1975b) of past sulfur oxides management policy in the Los Angeles area will help put many of these issues into perspective. When the nature of the Los Angeles smog problem was first investigated in the late 1940's, considerable attention was focused on the need for sulfur dioxide emission controls. In 1947, prior to the imposition of any discharge limitations, sulfur dioxide emissions in Los Angeles

[2] In recent years, that sulfate air quality standard would have been exceeded about one seventh of the time in Los Angeles.

County totaled about 680 tons per day, distributed among source categories as shown in Table 1.1 (Lemke, et al., 1969).

In 1947, the Los Angeles Air Pollution Control District (LAAPCD) adopted Rule 53 which limited sulfur compounds in exhaust gases from any source to 0.2 percent by volume (calculated as SO_2). By 1958, enforcement of this regulation had resulted in a lowering of total SO_2 emissions within the County to a level of 453 tons per day. The bulk of this initial reduction was achieved by removal of hydrogen sulfide from refinery gases prior to their combustion. Other refinery process operations were also affected. As shown in Figure 1.4, non-fuel-burning refinery process SO_2 emissions dropped sharply in 1957 and remained relatively unchanged thereafter over the next eighteen years.[3] Changes in sulfur dioxide emissions from refinery fuel burning are reflected in the "other" category of Figure 1.5.

In 1958, Rule 62 was adopted by the LAAPCD. The regulation prohibited the burning of any solid or liquid fuel containing over 0.5 percent sulfur by weight from May through November of the year, *provided that natural gas was otherwise available.* Rule 62 first went into effect in the summer of 1959. Referring to Figure 1.5, we note a steady drop in SO_2 emissions from fuel burning following adoption of Rule 62, reaching a relative minimum in about 1963.

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[3]Data on emission trends and projections used in Figures 1.4 through 1.7 were obtained from the Los Angeles Air Pollution Control District (1975b), and reflect historic records and forecasts through the close of 1974. Missing data were estimated by linear interpolation.

TABLE 1.1

Sulfur Dioxide Emissions in Los Angeles County for 1947
(Prior to Initial Emission Control Regulations)

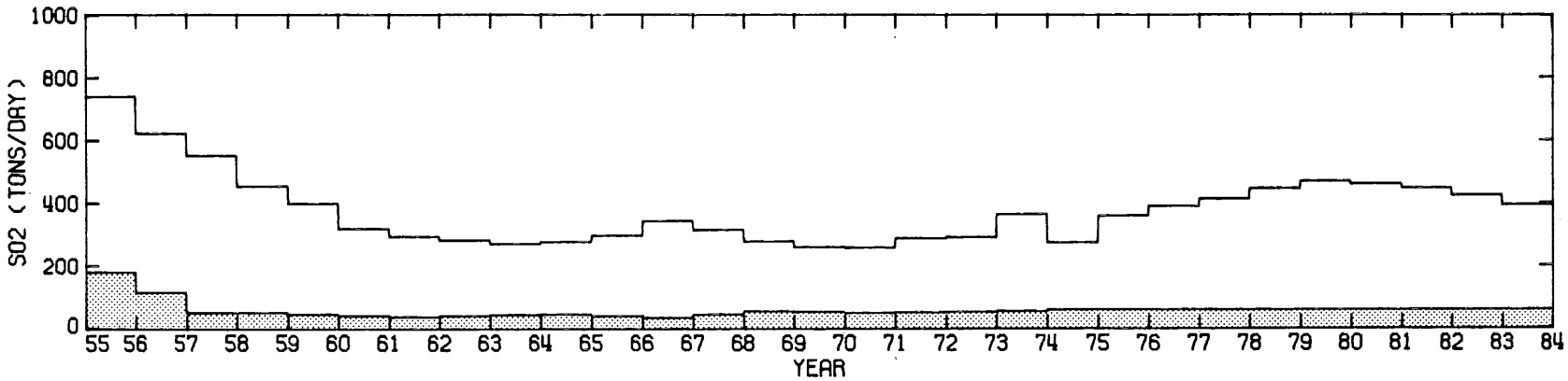
Source Class	SO_2 Emission Rate (Tons/Day)
(1) Combustion of Fuels Including: utility boilers refinery fuel industrial fuel	575
(2) Refinery Processes Operations	30
(3) Motor Vehicles	40
(4) Remaining Sources Including: chemical plants other stationary sources	35
TOTAL	680

Note: Emission values are taken from a graph presented by Lemke, et al. (1969). This graph could be read no more closely than ±5 tons/day.

FIGURE 1.4

SO2 EMISSIONS FROM PETROLEUM REFINING, PRODUCING AND MARKETING (SHADED)

VS. TOTAL SO2 EMISSIONS IN LA COUNTY, WITH LAAPCD FUTURE PROJECTION

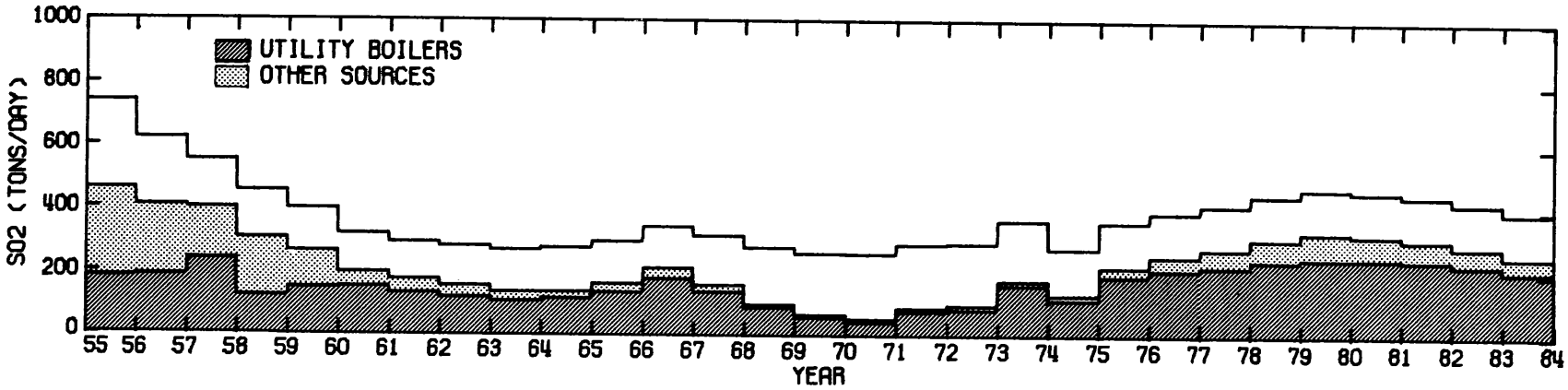


Reflects all SO_2 emissions from refinery processes except for fuel burning and sulfur recovery operations. Includes activities such as catalyst regeneration, waste water treatment, distillation losses, plus asphalt and coking operations.

FIGURE 1.5

SO2 EMISSIONS FROM FUEL BURNING SOURCES (SHADED) VS.

TOTAL SO2 EMISSIONS IN LA COUNTY, WITH LAAPCD FUTURE PROJECTION



The Other Sources category includes SO_2 emissions from fuel combustion by industrial, commercial, institutional, and residential sources. The projections shown above were based on emission control regulations in effect in 1975 which limited the sulfur content of fuel oil to 0.5% sulfur by weight. Emission control regulations have since been tightened to blunt some of the expected emissions increase indicated in this graph.

In spite of continued restrictions on the sulfur content of fuel, expansion of electric generating capacity in the Basin caused an increase in total SO_2 emissions beginning in about 1963. In January of 1964, Rule 62 was amended (by adoption of Rule 62.1) to make the sulfur content of fuel provisions applicable *year-round*. A limited supply of natural gas during the winter months rendered that change ineffective at slowing the growth in total emissions. These increasing emissions from stationary source fuel burning were eventually reversed in the late 1960's by importation of low sulfur fuel oil from Indonesia and southern Alaska, and by increased deliveries of natural gas. By October of 1968, Rule 62 was again amended to prohibit the burning of high sulfur fuel oil, *irrespective of natural gas supply conditions*. Shortly thereafter, natural gas deliveries began to diminish, with attendant substitution of low sulfur fuel oil leading to the upward trend in SO_2 emissions from fuel burning projected for Los Angeles County in the decade of the 1970's in Figure 1.5.

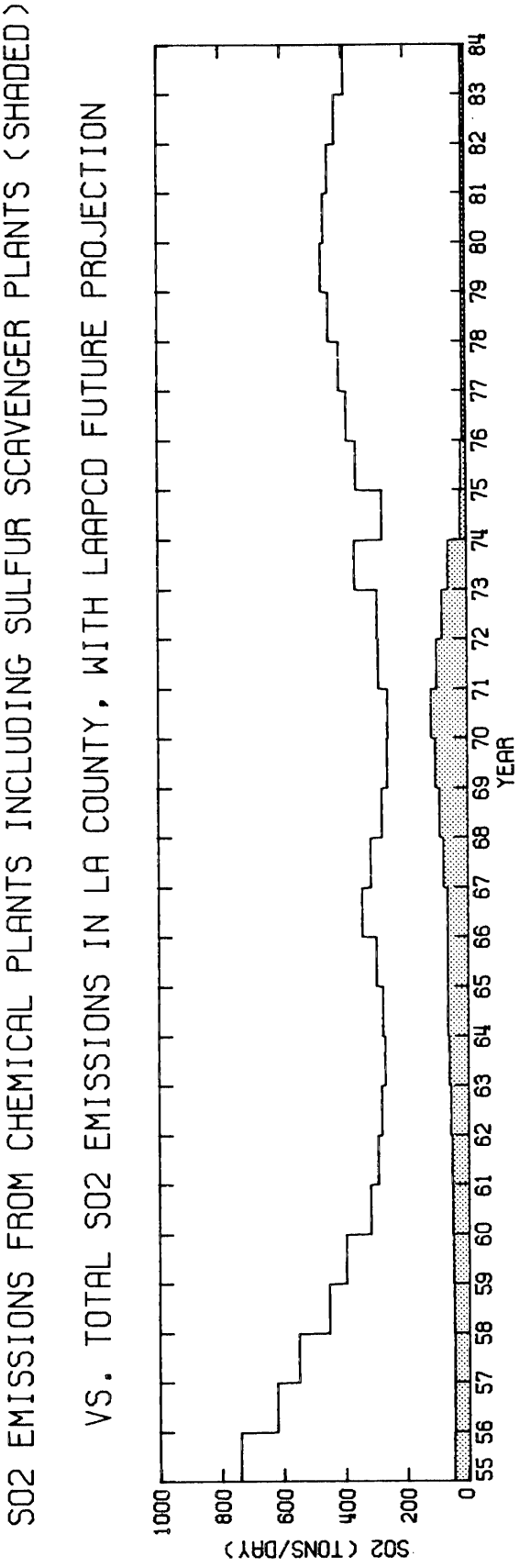
As a result of concern over increased sulfur oxides emissions from fuel burning activities, a further tightening of the sulfur content of fuel oil limitations became effective in early 1977. A fuel oil sulfur content of 0.25% by weight is not to be exceeded provided that such low sulfur oils are sufficiently available. That regulation is being reviewed at the present time, and may be modified within the next year. Fuel oil sulfur content limitations are in such a state of flux at the present time that this study will not attempt to anticipate the exact course of future events. The 0.5% sulfur content of fuel oil

limitation prevailing over the past two decades will be viewed as the baseline for our study, and further tightening of that standard will be considered to be a proper subject for control strategy analysis.

Another long-term feature of the SO_2 emission inventory for Los Angeles County is the emergence and subsequent control of substantial pollutant emissions from chemical process industries. In order to reduce emissions from refinery operations, sulfur-bearing refinery gases and acid sludge often were transported to adjacent plants which recovered elemental sulfur or sulfuric acid from the refinery effluent. These sulfur recovery operations were not one hundred percent efficient, and in time became major SO_2 sources in their own right. By 1970, Figure 1.6 shows that chemical processes accounted for 115 tons per day of SO_2 emissions, or nearly half of the total SO_2 emission inventory at that time. In 1971, Rule 53 was amended (effective 1973) to repeal certain exemptions previously granted to scavenger plants and to limit effluent streams from these plants to not more than 500 ppm of sulfur compounds calculated as SO_2. A maximum emission rate of not more than 200 pounds per hour of sulfur-bearing gases calculated as SO_2 was also imposed at that time. Figure 1.6 clearly shows the effect of these regulations on 1974 and subsequent SO_2 emission rates.

Automotive exhaust contains sulfur oxides derived from trace amounts of sulfur initially present in gasoline. California gasolines have traditionally been higher in sulfur content than the national average (Bureau of Mines, 1972 through 1975). As shown in Figure 1.7, SO_2 emissions from automobiles totaled about 35 tons per day in Los

FIGURE 1.6

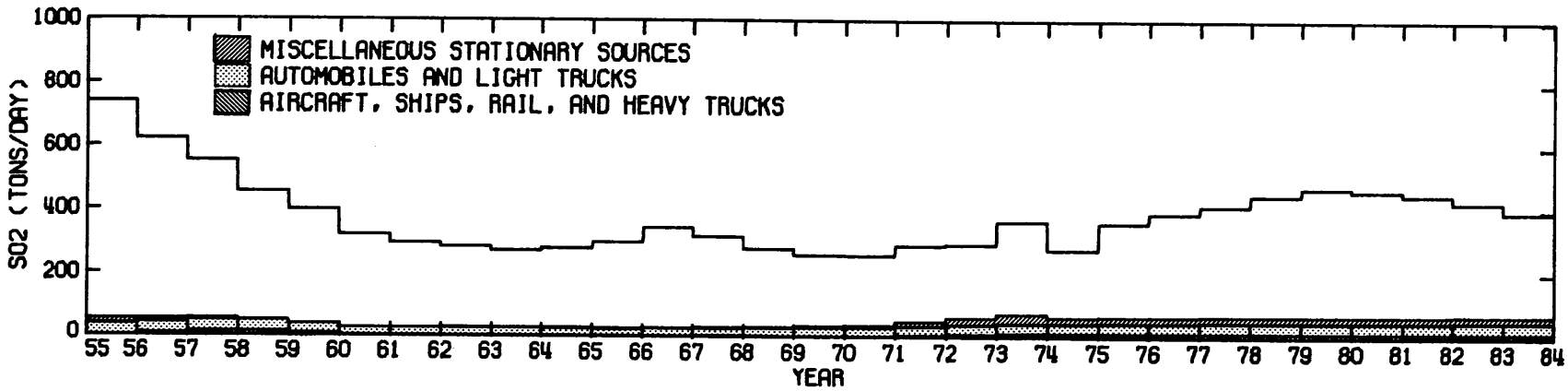


Includes sulfur recovery and sulfuric acid operations associated with petroleum refining.

FIGURE 1.7

SO2 EMISSIONS FROM MISCELLANEOUS SOURCES (SHADED) VS.

TOTAL SO2 EMISSIONS IN LA COUNTY, WITH LAAPCD FUTURE PROJECTION



Angeles County in the mid 1950's. Increased sophistication of refining operations permitted a decline in the sulfur content of local gasolines in the following decade. In spite of progressive increases in vehicle miles traveled yearly, automotive SO_2 emissions in Los Angeles County declined, reaching a minimum of 23 tons per day in 1965. By the early 1970's, increased gasoline consumption had returned sulfur dioxide emissions from automobiles to the vicinity of 30 tons per day. Although automotive SO_2 emissions represent only about 10 percent of the total SO_2 emission inventory, they are important to an understanding of Los Angeles sulfur oxides air quality for at least two reasons. First, automotive emissions occur at ground level where atmospheric dispersion is least effective at diluting the effluent prior to reaching receptor populations (and local air monitoring stations). Secondly, as automobile exhaust is passed over an oxidizing catalyst intended for hydrocarbon and carbon monoxide control, a fraction of the exhaust SO_2 is converted to sulfuric acid mist. The basin-wide air quality impact of incremental increases in primary sulfate emissions from automobiles is poorly quantified at present and can only be placed in perspective if viewed in the context of the local sulfate air quality problems arising from other sources.

Emissions from miscellaneous mobile and stationary sources in Los Angeles County are also shown in Figure 1.7. Miscellaneous stationary source SO_x emissions are presently dominated by calcining of petroleum coke produced by local refineries. Non-automotive mobile source emissions are dominated by highway use of diesel fuel and by combustion of high sulfur fuel oil by ships.

1.6.2 Sulfur Dioxide Air Quality Trends

Sulfur dioxide emissions undergo atmospheric transport, dilution, and removal processes resulting in the SO_2 concentrations measured at receptor air monitoring stations. Figure 1.8 displays the seasonal trends in SO_2 measurements over the past two decades at two such LAAPCD monitoring stations, Long Beach and downtown Los Angeles. Long Beach is chosen because it represents a location in the vicinity of major SO_2 sources in the harbor area. On the other hand, downtown Los Angeles is a commercial center located about 15 miles inland from the major coastal point sources of SO_2.

These ambient air quality graphs were generated by passing the time sequence of the LAAPCD's 24-hour average SO_2 readings over the period of interest through a linear digital filter.[4] The effect of this processing is to reveal long-term air quality trends by smoothing out fluctuations with frequency greater than four cycles per year, leaving the seasonal variations intact.

Referring to Figure 1.8, the following observations can be drawn. SO_2 air quality has improved since the mid 1950's at both Los Angeles and Long Beach. A sharp drop in SO_2 concentration occurred at both locations in 1959, at about the same time as the imposition of the initial controls on the sulfur content of fuel oil. From 1959 to 1963,

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[4]The filter's characteristics are such that it returns the low frequency signal with unit gain, half power cutoff set to remove disturbances with period shorter than three months, and roll-off at the half power point of 20 db per octave. For a discussion of digital filtering methods, see Bendat and Piersol (1971), Chapter 9.2.

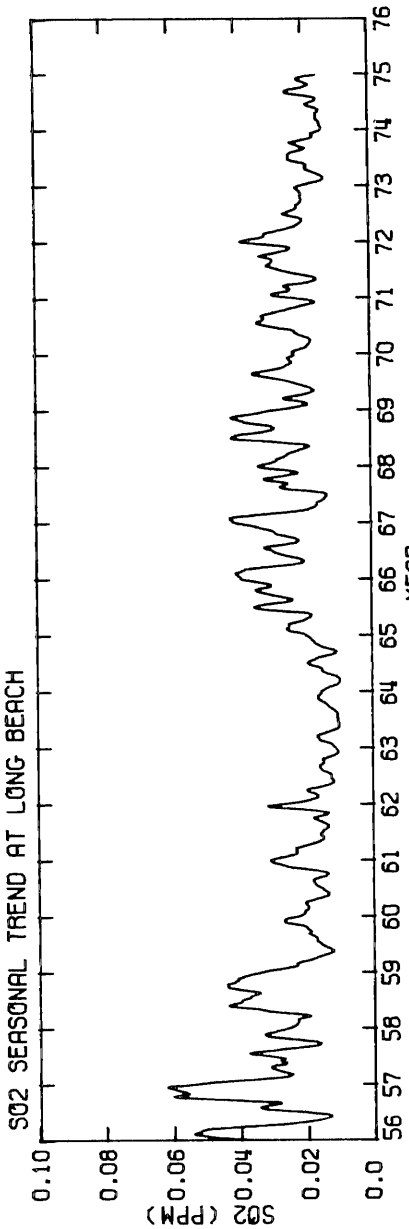

FIGURE 1.8(a)

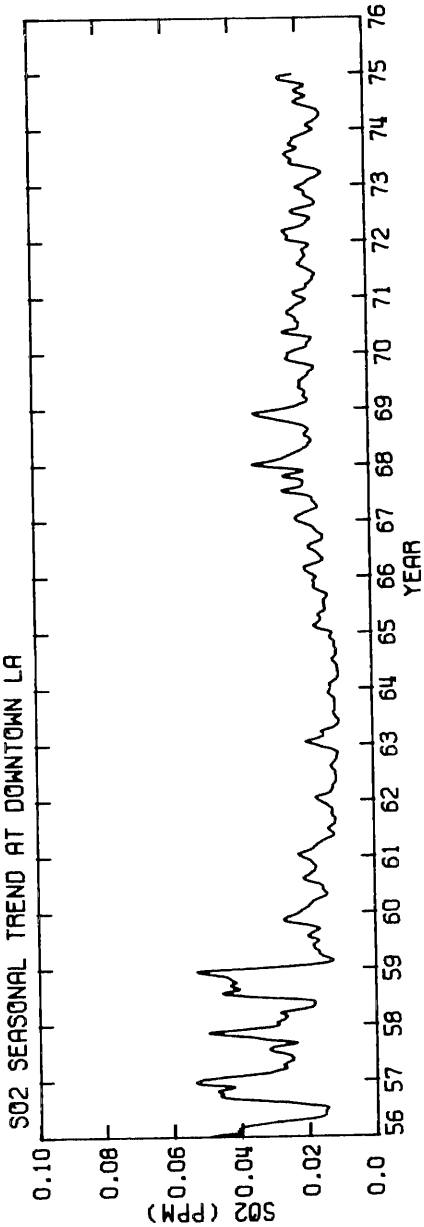

FIGURE 1.8(b)

air quality improved slightly at both locations, reaching a relative minimum in 1963 at the same time as the 1963 relative minimum in SO_2 emissions. SO_2 levels then rose, accompanying the subsequent late 1960's emission increases from chemical plants and automobiles. Since 1970, SO_2 concentrations at downtown Los Angeles have remained relatively constant, while at Long Beach a declining trend is apparent over the period 1972 through 1974 as nearby chemical plants installed new emission control equipment. Sulfur dioxide air quality is thus known to respond to changes in emission control regulations in a fairly predictable manner.

Successful past sulfur dioxide air quality control policies can be seen to have resulted from a sequential decision-making process. Growth in emissions from a single source class was observed. Emission control measures capable of containing the most pressing single problem at the moment were devised. Rapid feedback from atmospheric measurements confirmed that control strategies were working.

In the case of sulfate air quality, it would be hard to proceed with any degree of confidence to manage air resources by this traditional approach. The relative importance of various source classes to observed sulfate concentrations is a complex function of source location, meteorological conditions, atmospheric chemical reactions and long distance pollutant transport. Air monitoring data sufficient to deduce sulfate source-receptor relationships on the basis of response to past sulfur oxides control strategy changes probably do not exist. Analytical methods needed for an alternate approach to sulfate air quality management will be developed by this research.

CHAPTER 2

BASELINE AIR QUALITY CHARACTERIZATION: SULFATE AIR QUALITY IN THE SOUTH COAST AIR BASIN

2.1 Introduction

In preparation for an air quality control strategy study, we wish to characterize the readily observable features of sulfate air quality in the Los Angeles area. Design of a practical sulfate air quality modeling procedure requires that informed physical assumptions be made about the nature of the problem at hand. From this characterization, we hope to choose a modeling region which provides maximum opportunity to compare model calculations to historic observed air quality. The sulfate concentrations in air entering that modeling region will be specified, and an averaging time for the air quality model calculations will be selected. From spatial and temporal gradients in pollutant concentrations within the study region, generalizations will be drawn which impact the spatial and temporal resolution required of meteorological inputs to the modeling process. The evidence for chemical transformation of sulfur oxides within the Los Angeles atmosphere will be explored, and an approach to modeling the chemical conversion of sulfur dioxide to form sulfate will be selected.

Since historic sulfate and sulfur dioxide air quality data must be acquired and processed in order to address these issues, these data will be organized in passing so that they may be easily compared to future model calculations. Quality control checks will be applied to

the ambient data, and confidence intervals will be estimated for important parameters of the atmospheric measurements.

A rather comprehensive survey of the observed behavior of sulfur oxide air quality in the Los Angeles Basin thus will be undertaken. The objective is to select the bounds within which an air quality model relating sulfur oxides emissions to long-term average sulfate air quality might be specified with a reasonable chance for verifying its predictions.

2.2 Sulfate Air Quality in the South Coast Air Basin

2.2.1 Estimation of Sulfate Background Air Quality

On a global basis, over seventy percent of the emissions of sulfur compounds to the atmosphere arise from natural sources (Friend, 1973). These natural sources include sulfates from windblown sea salt, reduced sulfur compounds from biological decay, and emissions from volcanic activity. As a result of these natural sulfur sources, plus enrichment from man-made emissions, the global atmosphere contains low level "background" concentrations of sulfates, even at sites remote from major pollution sources.

The air entering the South Coast Air Basin thus contains non-zero levels of sulfate particulates which are not subject to further reduction by installation of controls on local emission sources. We wish to estimate these background concentrations so that they may be taken into account in our modeling exercise. The problem of estimating

South Coast Air Basin sulfate background levels has been treated by Hidy, et al., (1975) and by Trijonis, et al., (1975). Our discussion is built on much of the data used by these previous investigators.

The prevailing winds along the Southern California coast indicate that most new air masses entering the South Coast Air Basin are of marine origin. Early studies by Junge (1957) indicate that mid-Pacific marine air masses contain sulfate concentrations of the order of one microgram per cubic meter. "Giant particles" of a radius greater than 0.8μ were shown to contain the bulk of the sulfates at sea level in the Hawaiian Islands. Most of the sulfur content of these marine aerosols was traced back to the sulfate content of sea salt, although some ammonium sulfate of non-marine origin was also present. Sulfate concentrations due to sea salt were shown to decrease substantially with distance inland from the shore and with increasing altitude. More recent samples taken by Gillette and Blifford (1971) at a location about 250 km west of Santa Barbara, California showed particulate sulfur concentrations equivalent to about 0.72 $\mu gm/m^3$ of sulfate near the ocean's surface. A declining concentration with increasing altitude was also noted.

Moving closer to the South Coast Air Basin, there are indications that sulfate concentrations increase above the levels present in mid-ocean. Holzworth (1959) measured rather high total suspended particulate as well as sulfate concentrations at San Nicolas Island, the most remote of the Channel Islands off the Southern California coast (see Figure 2.1 or 2.3). More recent studies by Hidy, et al.,

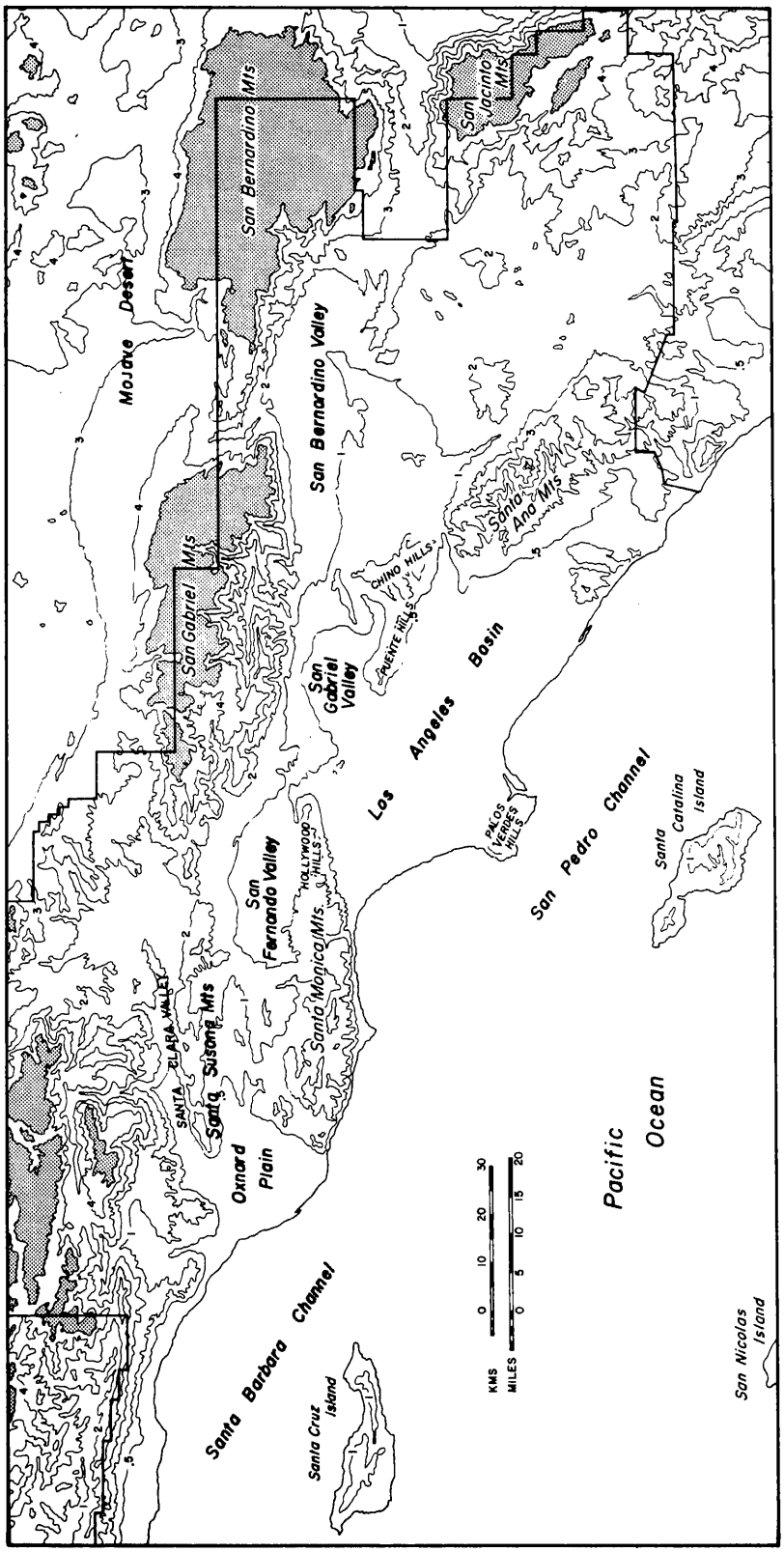

FIGURE 2.1
Topographic Map of Southern California
Showing the South Coast Air Basin in 1974

(1974), also measured air quality at San Nicolas Island but found sulfate concentrations more in line with what one would expect on the basis of the mid-ocean studies.

Hidy's group took thirteen sulfate samples on San Nicolas Island at an elevation of 200 meters above sea level. In Figure 2.2, the data of Hidy, et al., (1974) are plotted on log-probability paper along with all of the sulfate data of record taken by the Los Angeles Air Pollution Control District (LAAPCD) at downtown Los Angeles during the same time period, late July through early October 1970. A comparison of the statistics of these two data sets are given in Table 2.1. Methods used to estimate the parameters and confidence intervals shown in Table 2.1 are outlined in Appendix B4.

Geometric mean sulfate concentrations in incoming marine air averaged about a factor of four lower than those observed at downtown Los Angeles during the same season of 1970. The geometric standard deviation of the San Nicolas Island data is about the same as that of the inland observations. Thus while the air over the Channel Islands is noticeably less polluted than that at Los Angeles, extrapolation of the San Nicolas Island data would indicate that sulfate concentrations at remote locations exceeding the current California 24-hour average sulfate standard of 25 $\mu gm/m^3$ might be expected roughly one half of one percent of the time during the summer and fall seasons. In the absence of any more extensive marine air monitoring data, our modeling study will use the description of San Nicolas Island sulfate

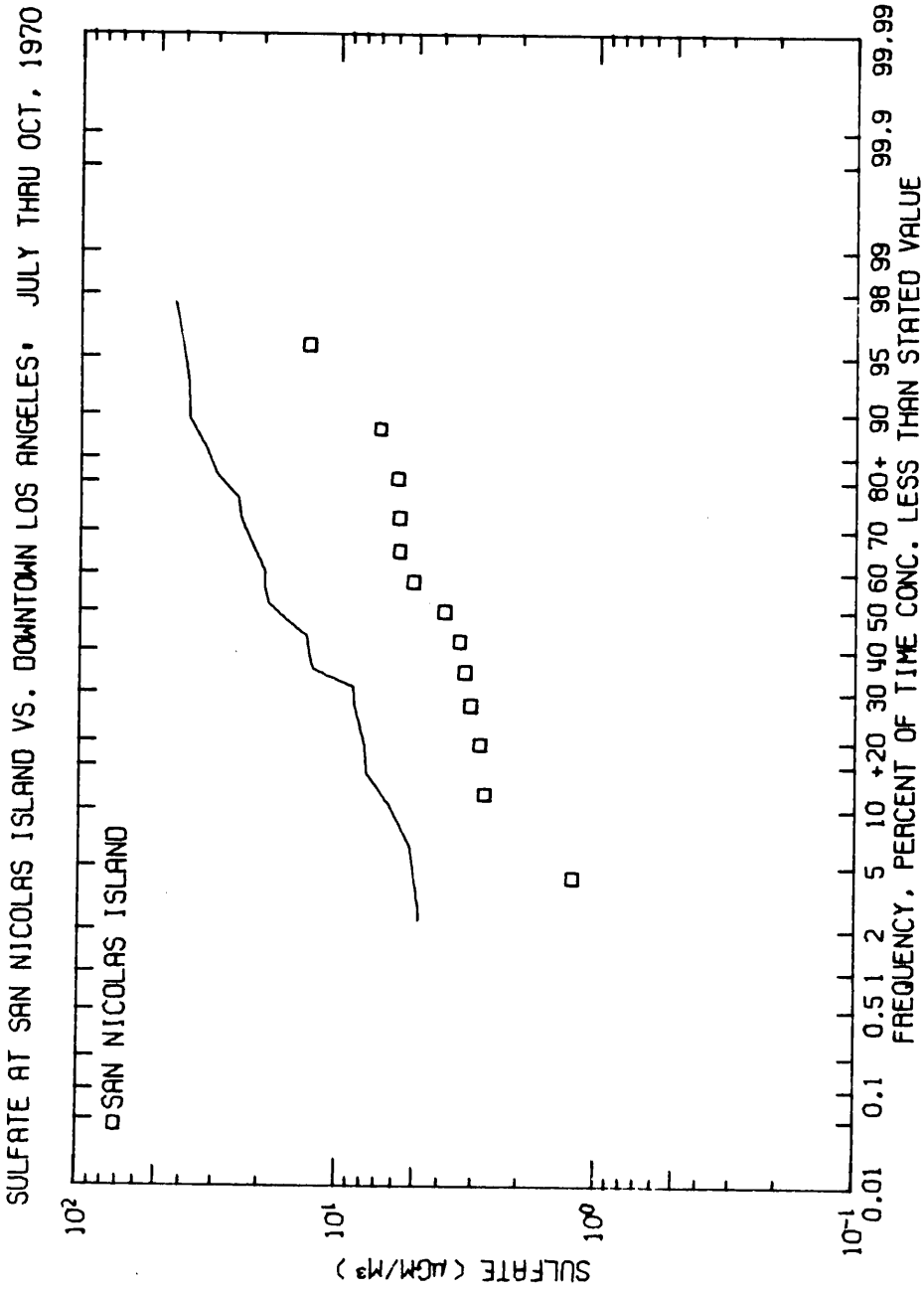
SULFATE AT SAN NICOLAS ISLAND VS. DOWNTOWN LOS ANGELES, JULY THRU OCT, 1970
SAN NICOLAS ISLAND
SULFATE (μGM/M3)
10^2
10^1
10^0
10^{-1}
0.01 0.1 0.5 1 2 5 10 +20 30 40 50 60 70 80+ 90 95 98 99 99.9 99.99
FREQUENCY, PERCENT OF TIME CONC. LESS THAN STATED VALUE

FIGURE 2.2

TABLE 2.1

Statistical Comparison of Sulfate Concentrations at San Nicolas Island vs. those at Downtown Los Angeles: Late July Through Early October, 1970

	ARITHMETIC STATISTICS					GEOMETRIC STATISTICS				
	SAMPLE ARITHMETIC MEAN $\bar{y}$	SAMPLE ARITHMETIC STANDARD DEVIATION σ	NUMBER OF SAMPLES n	LOWER CONFIDENCE LIMIT ON $\bar{y}$ (2.5 %ile)	UPPER CONFIDENCE LIMIT ON $\bar{y}$ (97.5 %ile)	ESTIMATED MEAN LOG α	ESTIMATED VARIANCE OF LOGS β^2	ESTIMATED GEOMETRIC MEAN μ_g	ESTIMATED GEOMETRIC STANDARD DEVIATION σ_g	ARITHMETIC MEAN ESTIMATED FROM α and β^2
Downtown Los Angeles	18.7	11.5	24	14.7	22.6	2.73	0.43	15.4	1.93	19.0
San Nicolas Island	4.9	3.0	13	3.4	6.4	1.44	0.33	4.2	1.78	5.0

(Units on arithmetic statistics are $\mu gm/m^3$)

air quality as given in Table 2.1 as one basis for estimation of sulfate concentrations in air entering the South Coast Air Basin.

While most new air masses entering the South Coast Air Basin are of marine origin, it is reassuring to note that even under desert breeze conditions, sulfate background concentrations will not deviate greatly from the background levels at San Nicolas Island. A number of monitoring programs have examined air quality in the Mojave Desert. The LAAPCD routine air monitoring station at Lancaster reported arithmetic mean sulfate levels of 3.1 $\mu gm/m^3$ for the last half of 1973 and 3.2 $\mu gm/m^3$ for calendar year 1974 (MacPhee and Wadley, 1975a, 1975b). At greater distances from the South Coast Air Basin, Gillette and Blifford (1971) measured particulate sulfur concentrations in Death Valley equivalent to about one microgram per cubic meter of sulfate.

The picture emerging from this analysis is as follows. At great distances from the South Coast Air Basin, either out to sea or well into the desert, sulfate concentrations appear to be about one microgram per cubic meter. Immediately adjacent to the air basin at San Nicolas Island or Lancaster, average sulfate concentrations are in the 3 to 5 $\mu gm/m^3$ range. We have seen that sulfate levels at downtown Los Angeles are substantially elevated above background. But what do the gradients in sulfate concentration look like within the Los Angeles Basin?

Note: As used throughout this study, the word "background" denotes pollutants present in air upwind of a source area of interest upon which the effect of emissions from within the source area will be superimposed. This regional background aerosol includes both natural emissions plus manmade material from distant sources.

2.2.2 Previous Surveys of Sulfate Air Quality Data in the Los Angeles Area

Within the past few years, a number of investigators (Tokiwa, et al., 1974; Trijonis, et al., 1975; Kurosaka, 1976) have surveyed the availability of sulfur dioxide and sulfate air quality data in the South Coast Air Basin. A composite listing of the data sources cited in these references plus some pioneer studies of historical interest are shown in Table 2.2, classified according to the purpose for which the sulfate air monitoring program was conducted.

Ideally, to define pollutant patterns over an air basin, one would like to have simultaneous observations on pollutant concentration at a large number of well spaced air monitoring locations. A high degree of temporal resolution in the data base would be desired. Sample analysis would be by comparable methods. Unfortunately, no single sulfate data base is available which provides long-term simultaneous sampling, basin-wide geographic coverage and high temporal resolution. The special studies mentioned in Table 2.2 often contain the most detailed information on diurnal sulfate concentration patterns. However, they do not attempt to provide a long-term continuous record over a wide-enough geographic area to allow one to draw many firm conclusions about spatial concentration gradients or seasonal pollutant trends. On the other hand, the routine 24-hour average sulfate air monitoring data gathered by local, state and federal agencies possibly satisfy at least two of our criteria. A large number of widely spaced monitoring sites exist and the sampling histories at these sites stretch over long periods of time. The 24-hour average temporal resolution of

TABLE 2.2

SOURCES OF SULFATE AIR QUALITY DATA IN THE SOUTH COAST AIR BASIN
(through 1974)

A. Routine Air Monitoring Programs in Operation in 1974 (List Compiled by Kurosaka, 1976)

Agency	Number of Stations in South Coast Air Basin(1974)	Sulfate Sampling/ and Analysis Method (1974)***	Sulfate Data Averaging Time	SO_2 Sampling Method	SO_2 Data Averaging Time	Sampling History
Los Angeles Air Pollution Control District (LAAPCD)*	7	Hi-Vol/Turbidimetric	24 hour	conductometric	1 hour	1965-Present
San Bernardino Air Pollution Control District*	8	Hi-Vol/Turbidimetric	Quarter Year Composite	conductometric	1 hour	1965-Present
Riverside Air Pollution Control District*	1	Hi-Vol/Turbidimetric	24 hour	conductometric	1 hour	1974-Present
National Air Surveillance Network (NASN)	11	Hi-Vol/Methylthymol Blue	24 hour	West-Gaeke	24 hour	Mid 1950's-Present
Community Health and Environmental Surveillance System (CHESS)	6	Hi-Vol/Methylthymol Blue	24 hour	West-Gaeke	24 hour	1972-Present

B. Recent Special Studies (List compiled by Kurosaka, 1976)

Study Title and Investigators' Affiliation						
Aerosol Characterization Experiment (ACHEX)	Rockwell International Science Center*	Variety of methods compared	2 hour and 24 hour	flame photometric		several days during 1972-1973
California Air Resources Board Monitoring Program	California Air Resources Board	Low-Vol filter/X-Ray fluorescence	2 hour			1973 to present
Regional Monitoring of Smog Aerosols	U.C. Davis**	Lundgren Impactor ion-excited X-Ray emission		NONE		1973 to present
Sulfur Dioxide Conversion Study	Caltech	flash vaporization	1 hour	flame photometric		several days, 1973

C. Recent Studies of Freeway Air Quality (List Compiled by Kurosaka, 1976)

Impact of Motor Vehicle Exhaust catalysts on Air Quality	Rockwell International AIHL, U.S. Navy**	Variety of methods compared	2 hour			1974 to present
Los Angeles Catalyst Study	U.S. EPA	Hi-Vol/?	4 hour and 24 hour			1974 to present
Air Resources Board Freeway Monitoring Study	California Air Resources Board	Low-Vol filter/X-Ray fluorescence	2 hour			1975 to present
		Hi-Vol?	24 hour			

D. Additional Sources of Sulfate Data in or near the South Coast Air Basin (Data taken prior to 1972)

Reference						
Renzetti et.al, (1955) (Air Pollution Foundation)		Hi-Vol/Turbidimetric	24 hour	conductometric		Aug. thru Nov. 1954
Holzworth, (1959) (U.S. Weather Bureau)		Hi-Vol/Turbidimetric	24 hour	NONE		May, 1956 - Jan. 1957
Thomas, (1962)		Conductometric	30 minutes	conductometric		several weeks 1961
Los Angeles APCD "Sulfur Trioxide" Monitoring Program		Conductometric	1 hour	conductometric	1 hour	1963-1969
Gillette and Blifford, (1971)		Impactor/X Ray fluorescence	1 hour	NONE		1967
Lundgren, (1970)		Impactor & Filters/ Turbidimetric	4 hour and 24 hour	NONE		Nov, 1968
Hidy, et.al, (1974)		Hi-Vol & Low-Vol/ Turbidimetric	24 hour	NONE		Jul- Oct. 1970

*Now part of the Southern California Air Pollution Control District

**Sponsored by the California Air Resources Board

***While X-Ray fluorescence is listed as a mean of sulfate determination, the actual measurement made in that case is for total particulate sulfur.

these monitoring programs, while not as refined as some special studies, is still short when compared to our objective of defining seasonal trends. This baseline air quality characterization will first focus on the nature of the available sulfur oxides routine air monitoring data.

2.2.3 Routine Air Monitoring Programs for Sulfates and Sulfur Dioxide in the South Coast Air Basin

During the period 1972 through 1974, the APCD, CHESS and NASN air monitoring programs listed in Table 2.2 operated concurrently. Each agency sampled for both sulfur dioxide and suspended particulate sulfates. If these data bases could be pooled, measurements at over two dozen monitoring sites would be available against which to compare air quality model calculations. Thus the years 1972 through 1974 will be chosen as the base years for our study.

But the question remains, "To what extent were the sampling methods used by these agencies comparable?" In Appendix B1 to this report, each of these air monitoring programs has been described in an attempt to isolate differences in experimental design. It is found that ideally the sulfate air quality monitoring methods used by each of these agencies should be comparable. However, the CHESS network encountered some analytical problems in practice and a correction factor must be applied to some of their data. Sulfur dioxide monitoring methods used by the LAAPCD are judged to be significantly different from those of CHESS and NASN. Some important implications of these

differences in sulfur dioxide sampling methodology will become apparent as our investigation proceeds.

Figure 2.3 indicates the location of sulfate air quality monitoring stations operated in or near the South Coast Air Basin during the period 1972 through 1974. Since the validity of the San Bernardino County APCD sulfate data during those years has been questioned (Kurosaka, 1976), only stations operated by the Los Angeles Air Pollution Control District, EPA's CHESS program, and the National Air Surveillance Network are shown. Steps taken to acquire and prepare data from these air monitoring stations for comparative analysis are outlined in Appendix B2.

2.2.4 Long-Term Average Sulfate Air Quality

Concentration averages given in Figure 2.4 represent the arithmetic mean of sulfate concentrations for all days of record at the CHESS, LAAPCD and NASN monitoring stations during the years 1972 through 1974. It is seen that long-term average sulfate levels are of the same order of magnitude over most portions of the South Coast Air Basin. Concentrations appear higher than average in the San Fernando Valley and lower than average at the western-most and southern-most monitoring sites. These deviations from the basin-wide mean of 11.7 $\mu gm/m^3$ are still small, perhaps $\pm$ 3 $\mu gm/m^3$. But how much uncertainty is associated with these concentration averages? Is that uncertainty larger than the differences in average sulfate concentration computed at separate monitoring sites? How many samples must one average in

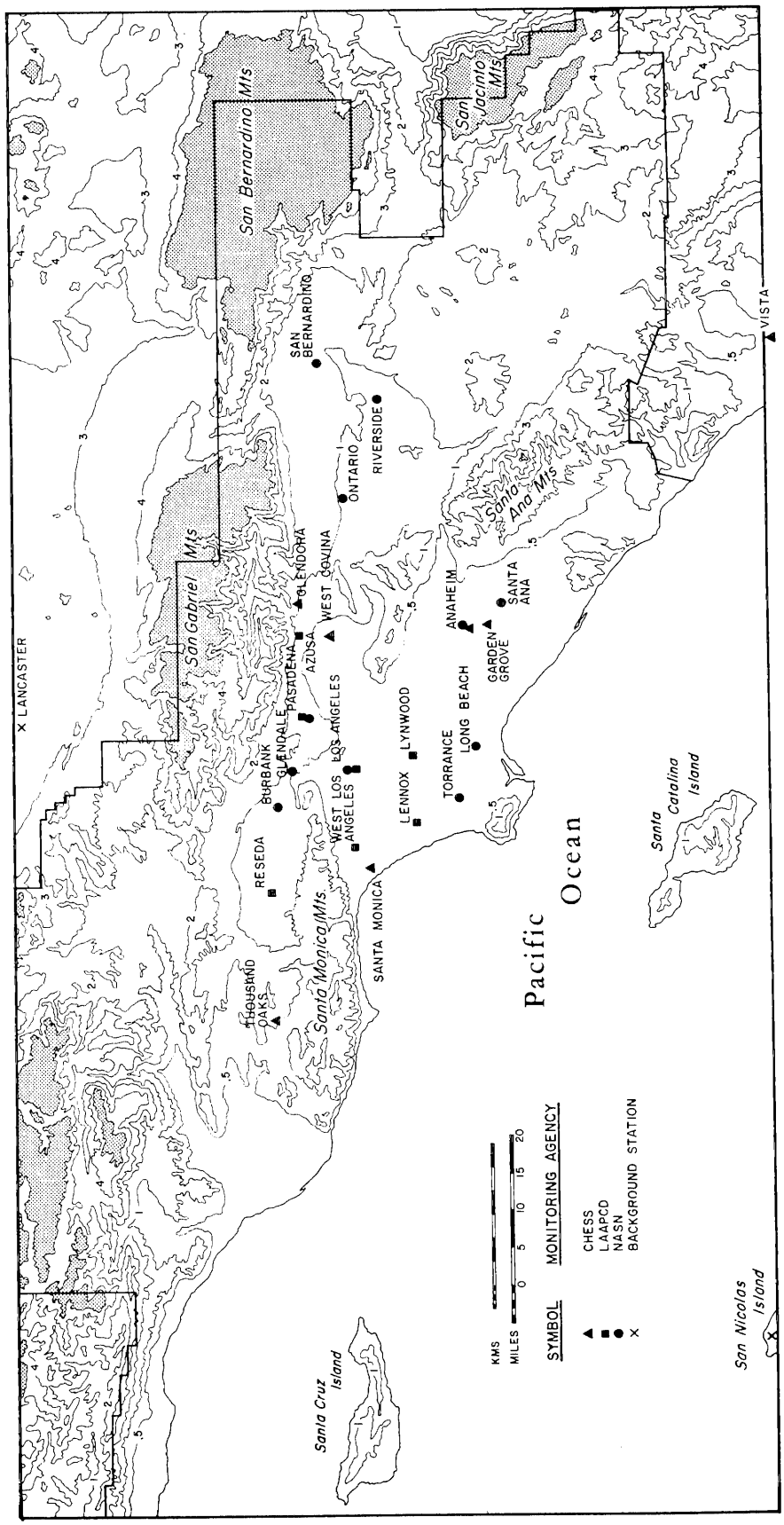

FIGURE 2.3

Sulfate Air Quality Monitoring Sites in or near the South Coast Air Basin

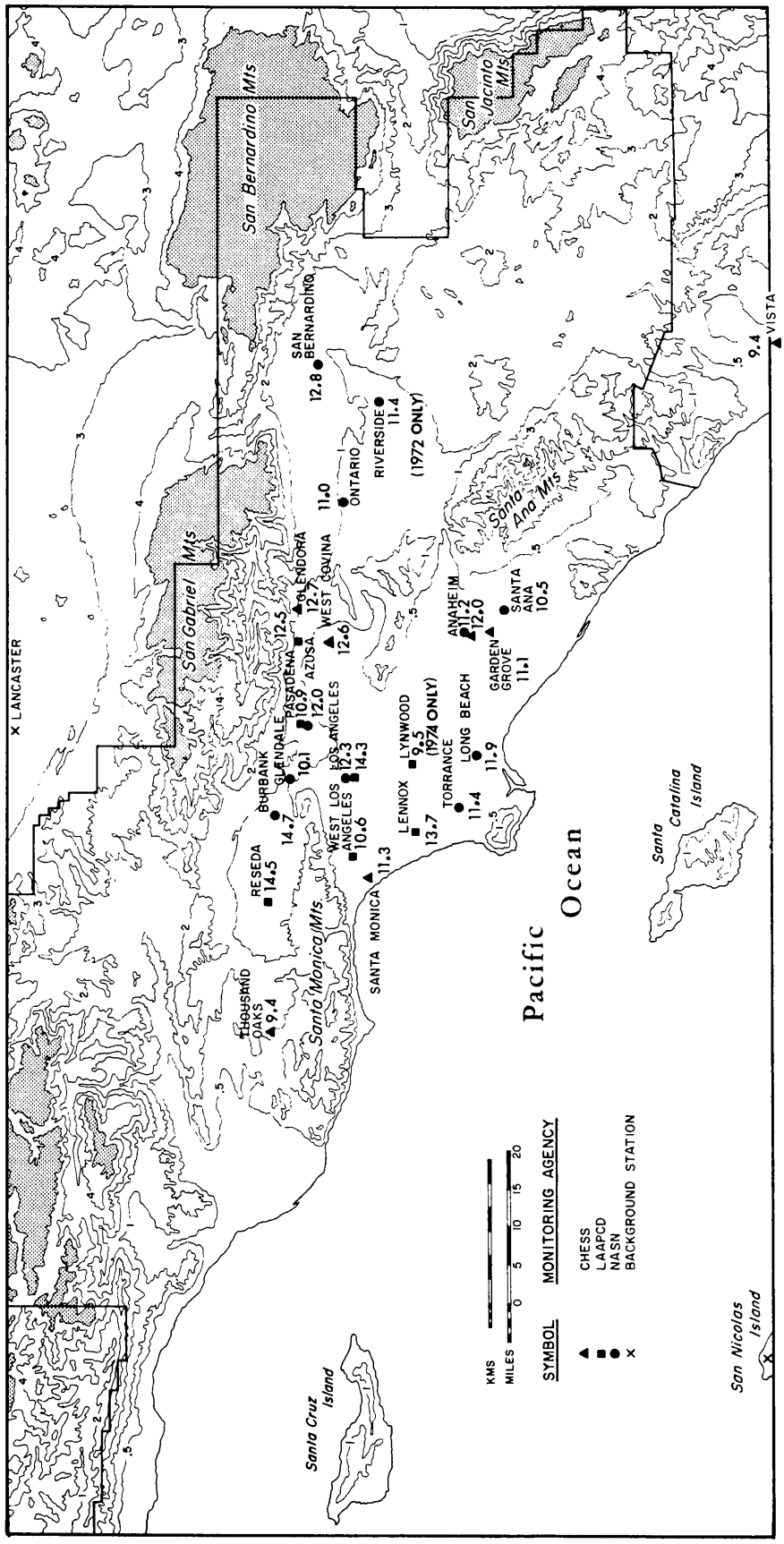

FIGURE 2.4

Arithmetic Mean Sulfate Air Quality: 1972 through 1974
Concentrations Shown Adjacent to Monitoring Site Location in $\mu gm/m^3$

order to make useful statements about differences in sulfate levels from one time period to the next? The complexity and averaging time chosen for our air quality model will depend on the outcome of those inquiries.

One way to approach answering these questions is to examine the statistical sampling distribution of the air quality measurements made at individual air monitoring stations. Empirical work pioneered by Larsen (1971) suggests that air quality measurements approximately follow a simple two parameter log-normal distribution for all pollutants and all averaging times. An exception to this rule of thumb often occurs when minimum detection limit problems distort pollutant measurements made at low concentrations. A quick visual check on the log-normality assumption as it applies to our sulfate air quality data is provided in Figures 2.5, 2.6, and 2.7. These three figures represent log-probability plots of sulfate concentration measurements made over the period 1972 through 1974 at typical NASN, LAAPCD, and CHESS air monitoring stations, respectively. It can be seen that the cumulative distribution of the sulfate data plots as a nearly straight line at sulfate concentrations above 2 $\mu gm/m^3$, indicating that the data indeed approximately fit a two parameter log-normal distribution in that range. At the CHESS and LAAPCD stations, the lower tails of the distribution sag noticeably at concentrations below 2 $\mu gm/m^3$, while values in that range are unavailable at the NASN station. The departure from two parameter log-normality by the LAAPCD data at very low sulfate concentrations could well be due to the measurement problems at low

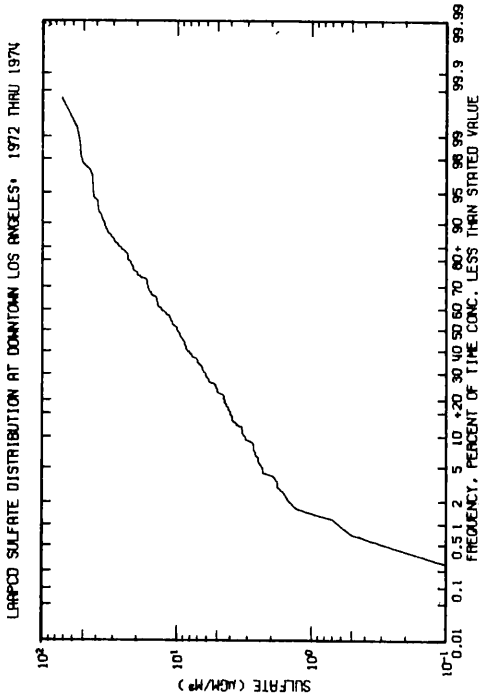

FIGURE 2.6

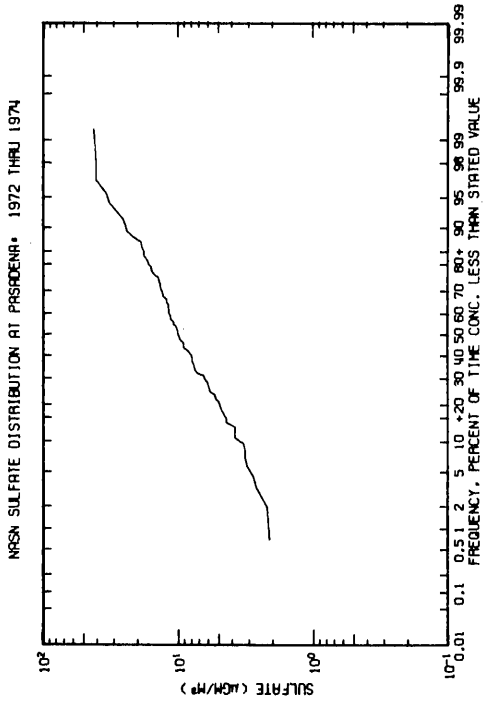

FIGURE 2.5

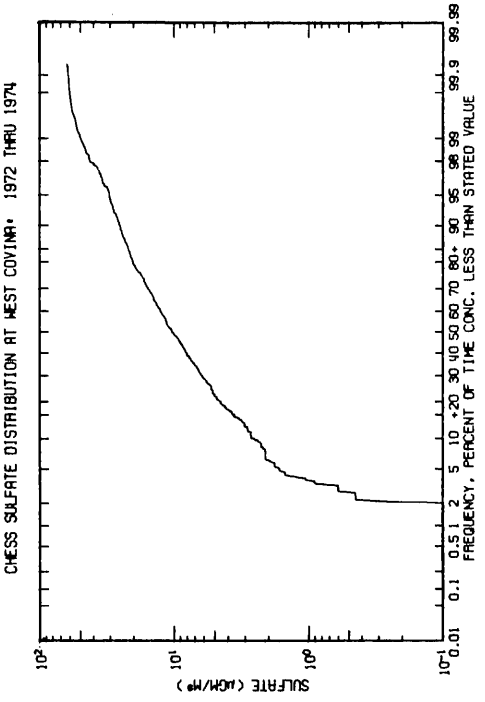

FIGURE 2.7

concentrations reported by Porter, et al. (1976). A similar but previously unreported problem may have affected the CHESS monitoring program. *In any case, the absolute magnitude of the sulfate concentration by which these samples deviate from a simple two parameter log-normal distribution at low concentrations is extremely small.* A complete set of graphs showing the cumulative distribution of the sulfate data at each of the monitoring stations under consideration is given in Appendix B3. In general, the smoothest, straightest lines on log-probability paper occur at stations with the greatest number of observations. Cumulative distributions at NASN stations with relatively few observations (e.g. Riverside with 18 samples) would seem to be a bit lumpy. This is to be expected at small sample sizes.

Table 2.3 shows some pertinent statistics of the observations at sulfate air monitoring stations over the period 1972 through 1974. Estimates of the mean natural log, α, and variance, β^2, of the natural logs of the sulfate observations are given in that table. Parameter estimation procedures are outlined in Appendix B4.

Our intended air quality modeling effort will later result in calculation of arithmetic mean sulfate concentration patterns over portions of the South Coast Air Basin. If we are to compare model results to field observations, it becomes important to be able to place confidence intervals around the arithmetic mean calculated from a given set of sulfate air quality data. Approximate 95% confidence

TABLE 2.3

Statistical Description of Sulfate Air Quality Data in the South Coast Air Basin: 1972-1974

		ARITHMETIC STATISTICS					GEOMETRIC STATISTICS				
		SAMPLE ARITHMETIC MEAN $\bar{y}$	SAMPLE ARITHMETIC STANDARD DEVIATION σ	NUMBER OF SAMPLES n	LOWER CONFIDENCE LIMIT ON $\bar{y}$ (2.5 %ile)	UPPER CONFIDENCE LIMIT ON $\bar{y}$ (97.5 %ile)	ESTIMATED MEAN LOG α	ESTIMATED VARIANCE OF LOGS β^2	ESTIMATED GEOMETRIC MEAN μ_g	ESTIMATED GEOMETRIC STANDARD DEVIATION σ_g	ARITHMETIC MEAN ESTIMATED FROM α and β^2
THOUSAND OAKS	CHESS	9.41	9.08	890.00	9.08	9.73	1.87	0.83	6.48	2.48	9.80
RESEDA	LAAPCD	14.53	16.59	214.00	12.53	16.53	2.09	1.31	8.11	3.14	15.62
SANTA MONICA	CHESS	11.27	8.82	840.00	10.91	11.62	2.16	0.57	8.64	2.13	11.50
WEST LA	LAAPCD	10.64	9.51	215.00	9.49	11.78	1.97	0.86	7.19	2.53	11.04
LENNOX	LAAPCD	13.71	10.76	219.00	12.43	14.99	2.32	0.64	10.19	2.22	14.00
TORRANCE	NASN	11.40	6.59	83.00	10.04	12.77	2.29	0.29	9.84	1.72	11.40
LONG BEACH	NASN	11.94	7.65	79.00	10.31	13.57	2.33	0.27	10.28	1.68	11.78
LYNWOOD	LAAPCD	9.47	8.55	68.00	7.50	11.44	1.87	0.81	6.46	2.46	9.71
BURBANK	NASN	14.73	18.66	90.00	11.03	18.43	2.37	0.53	10.68	2.07	13.93
GLENDALE	NASN	10.12	7.70	71.00	8.39	11.86	2.08	0.47	8.02	1.99	10.16
LOS ANGELES	NASN	12.33	9.17	83.00	10.43	14.23	2.29	0.44	9.87	1.95	12.32
LOS ANGELES	LAAPCD	14.29	12.63	212.00	12.76	15.83	2.29	0.80	9.89	2.44	14.72
PASADENA	LAAPCD	10.94	10.73	214.00	9.64	12.23	1.94	0.99	6.93	2.71	11.38
PASADENA	NASN	12.00	8.97	79.00	10.09	13.91	2.24	0.50	9.43	2.03	12.10
GARDEN GROVE	CHESS	11.08	7.53	898.00	10.80	11.37	2.19	0.47	8.97	1.98	11.32
ANAHEIM	CHESS	11.37	8.34	966.00	11.10	11.65	2.20	0.52	8.99	2.06	11.68
ANAHEIM	NASN	11.15	7.85	83.00	9.52	12.78	2.20	0.44	9.04	1.94	11.25
SANTA ANA	NASN	10.51	8.21	83.00	8.81	12.21	2.16	0.34	8.68	1.79	10.30
AZUSA	LAAPCD	12.55	11.37	215.00	11.18	13.91	2.12	0.92	8.35	2.61	13.22
WEST COVINA	CHESS	12.57	9.93	881.00	12.20	12.95	2.23	0.69	9.27	2.29	13.07
GLENDORA	CHESS	12.66	10.58	937.00	12.31	13.02	2.20	0.76	9.02	2.40	13.22
ONTARIO	NASN	10.99	7.86	64.00	9.12	12.87	2.16	0.49	8.64	2.02	11.06
RIVERSIDE	NASN	11.40	6.54	18.00	8.40	14.40	2.29	0.33	9.92	1.78	11.71
SAN BERNARDINO	NASN	12.80	10.70	75.00	10.46	15.14	2.25	0.64	9.47	2.22	13.04
VISTA	CHESS	9.45	7.06	1035.00	9.25	9.65	2.00	0.53	7.40	2.07	9.65

intervals on the three year arithmetic mean sulfate concentration at each monitoring station are given in Table 2.3. The confidence interval estimation procedure is detailed in Appendix B4.

The confidence intervals on the three year arithmetic mean sulfate concentrations overlap at most monitoring sites. For example, confidence intervals at fourteen of the twenty-five monitoring sites would contain the basin-wide mean value of 11.7 $\mu gm/m^3$. Of the remaining eleven stations, three miss containing that value by less than 0.3 $\mu gm/m^3$, which is probably less than the uncertainty introduced by the approximations made when calculating the confidence intervals. Average sulfate values at the margins of our study area, at Vista and Thousand Oaks, are significantly lower than those at stations in the central portion of the Los Angeles basin. Distinctly higher values than average are reported at Lennox in the immediate vicinity of some major SO_2 sources. High values are also found in the San Fernando and the eastern San Gabriel Valleys. Even these relative "hot spots" differ from the concentrations reported elsewhere in the central portion of the air basin by about the same amount as the differences between sulfate averages found by two different monitoring agencies at the same location, downtown Los Angeles.

These comparisons of long-term concentration averages plus the previous discussion of off-shore and desert sulfate air quality lead to three important physical generalizations:

Generalization 1: Long-run average sulfate concentrations are about the same at monitoring sites in the central portion of the South Coast

Air Basin (i.e. about 11.7 micrograms per cubic meter over our three base years).

Generalization 2: The lowest sulfate concentrations observed are systematically found at the margins of our study area (e.g. at San Nicolas Island, Lancaster, Thousand Oaks, and Vista).

Generalization 3: Los Angeles sulfate air quality is significantly elevated above background sulfate concentrations in incoming marine or desert air.

2.2.5 Seasonal Trends in Sulfate Concentration in the South Coast Air Basin

Sulfate concentrations observed at the downtown Los Angeles station of the LAAPCD during the past decade are shown in time series in Figure 2.8. Concentration fluctuations from day to day are quite large, with high values occurring at least occasionally in all seasons of the year. However, the data can be smoothed to reveal seasonal trends, as shown in Figure 2.9.

The graph in Figure 2.9 was generated by passing the time sequence of 24 hour average sulfate readings over the period of interest through a linear digital filter.[1] The effect of this processing is to reveal long-term air quality trends by suppressing fluctuations with frequency greater than four cycles per year, leaving seasonal variations intact.

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[1] The filter's characteristics are such that it returns the low frequency signal with unit gain, half power cutoff set to remove disturbances with period shorter than three months, and roll off at the half power point of 20 db per octave. For a discussion of digital filtering methods see Bendat and Piersol (1971), Chapter 9.2.

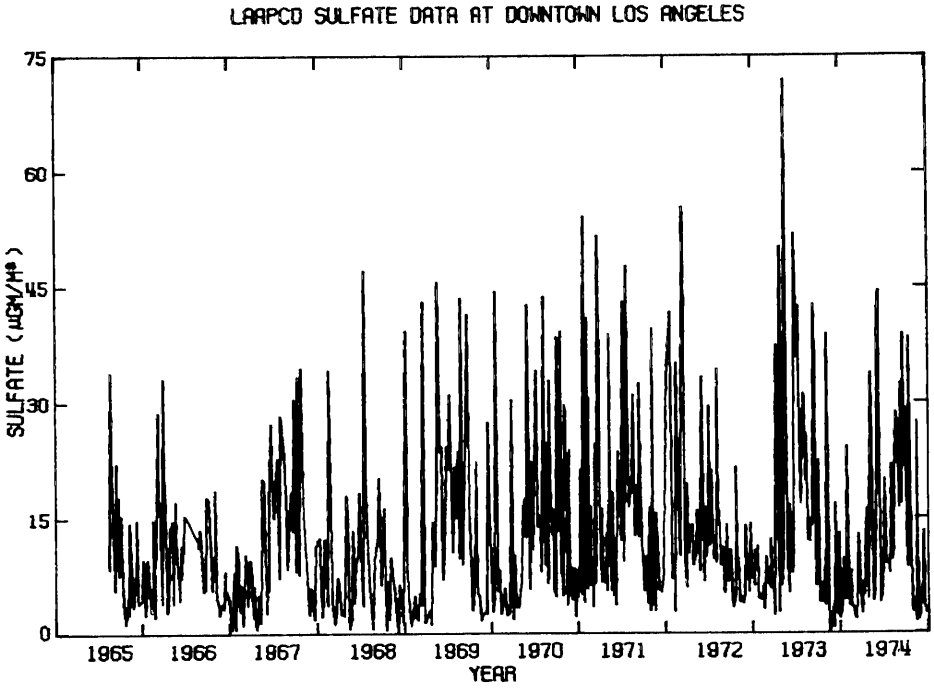

FIGURE 2.8

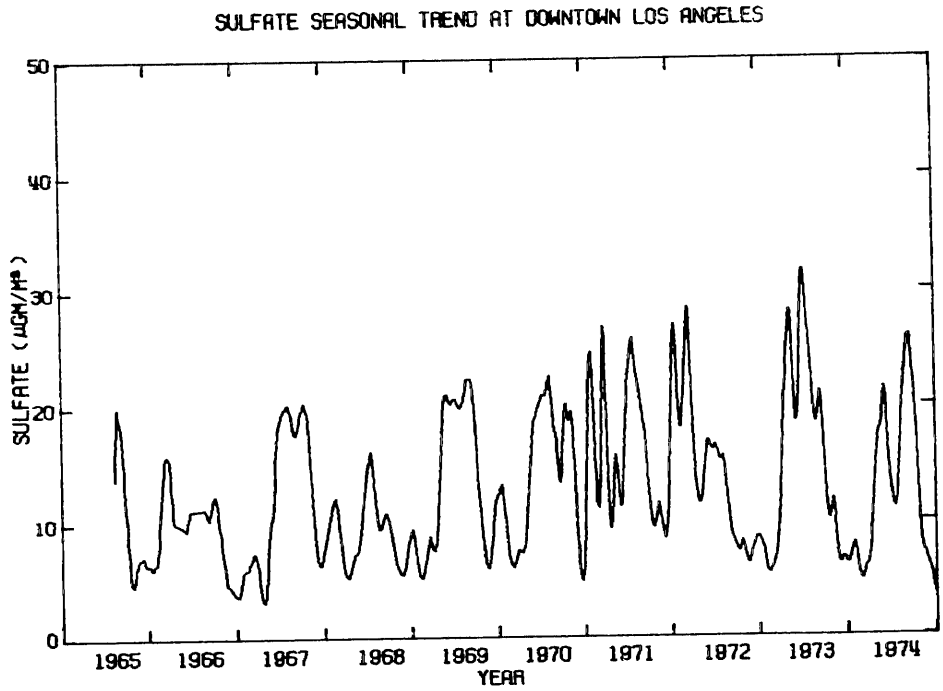

FIGURE 2.9
(From Cass, 1975)

It is apparent from Figure 2.9 that measured sulfate levels at downtown Los Angeles have risen over the past decade, reaching a relative peak in 1973. A small decline followed in 1974. Both the annual mean and upper bound of seasonal maxima follow this trend. There is a broad summer seasonal peak in sulfate levels apparent in most years of record. A wintertime peak is also apparent, but its magnitude varies greatly from year to year. In the winters of 1972-73 and 1973-74, for example, the winter peak was very small and confined to a few weeks around the first of the year, while in the winters of 1970-71 and 1971-72 the winter peak was characterized by isolated days of very high sulfate levels which led to elevated annual averages for those years.

In Figure 2.10, the same filtering process has been applied to the LAAPCD and CHESS sulfate data at all monitoring stations active during the period 1972 through 1974. The resulting graphs are positioned on a map of the South Coast Air Basin in close proximity to each station's physical location. National Air Surveillance Network data were not presented because their infrequent monitoring schedule provides insufficient data for this sort of treatment. The graphs in Figure 2.10 are small and thus difficult to read. They have been reproduced at a larger scale in Appendix B5.

The similarity of seasonal pollutant patterns at all monitoring stations is quite striking. The timing and relative magnitude of seasonal concentration peaks and troughs is apparently related from

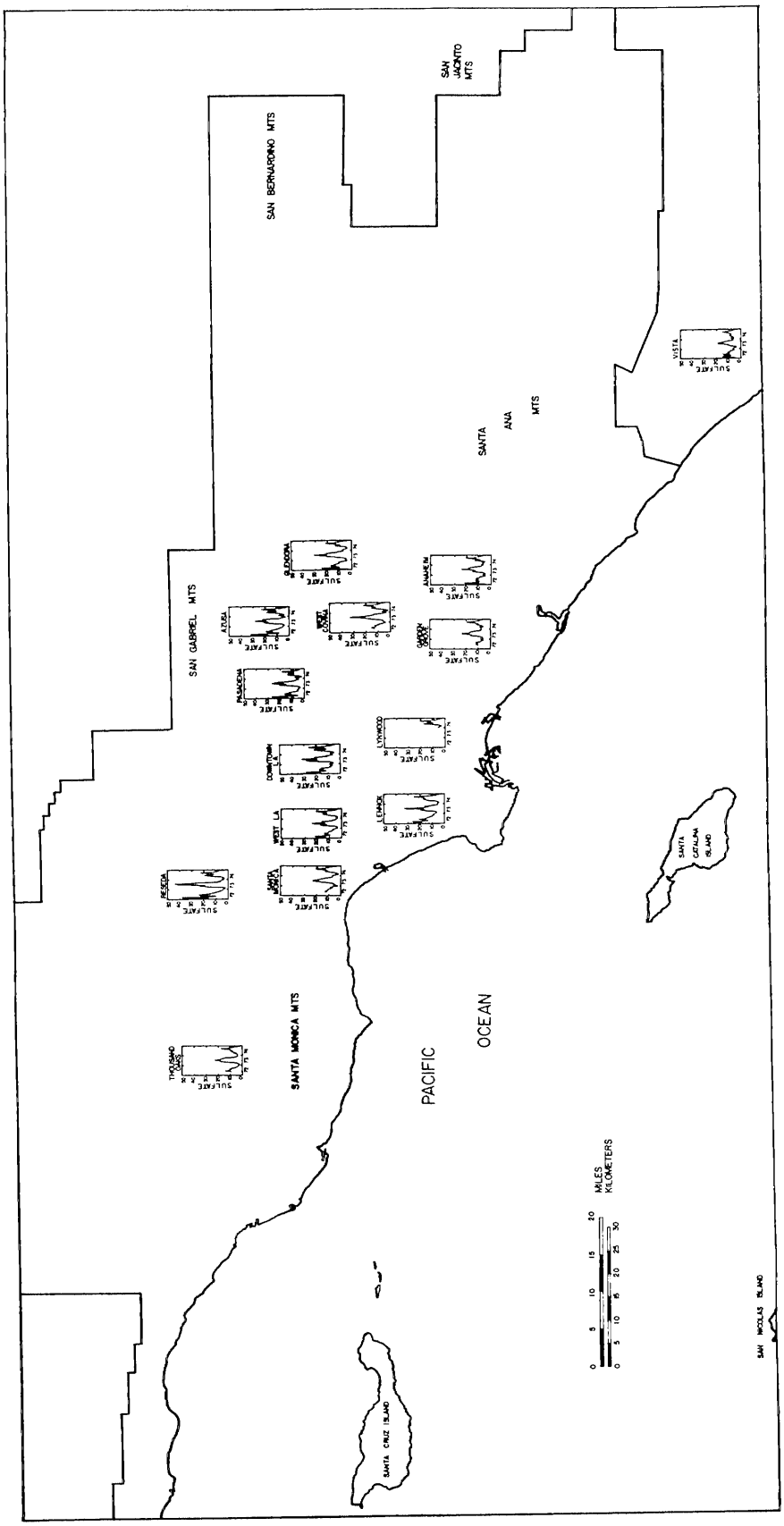

FIGURE 2.10
Seasonal Trends in Sulfate Air Quality 1972 through 1974

Thousand Oaks to the northwest to Vista on the south, a distance of nearly two hundred kilometers.

2.2.6 A Comparison of Simultaneous 24-Hour Average Sulfate Air Quality Measurements

Two features noted so far are that long-run average sulfate concentrations in the central portion of the air basin are fairly uniform, and similar seasonal modulation of those concentration levels appears to be applied basin-wide. We will now find something even more interesting. This organized behavior is manifested to a large degree on a day-to-day basis.

Figures 2.11 and 2.12 show the relationship between sulfate levels measured at Lennox, downtown Los Angeles, and Pasadena on the same days during the years 1972 through 1974. These three monitoring sites lie approximately along a resultant sea breeze wind trajectory stretching from a major SO_2 source area at the coast through the central business district and into inland valleys beyond, as shown by comparing Figure 2.3 with Figures 2.13 and 2.14. Sulfate values are approximately the same at all three locations on the same day, as shown by the unit slope and near zero intercept of the regression lines describing the best fit relationship between sulfate values at pairs of stations.

But how widespread is this tracking of daily sulfate concentration changes? Tables 2.4 and 2.5 show the log-linear correlation between sulfate concentrations reported at pairs of monitoring stations for the same day, plus the number of simultaneous observations available

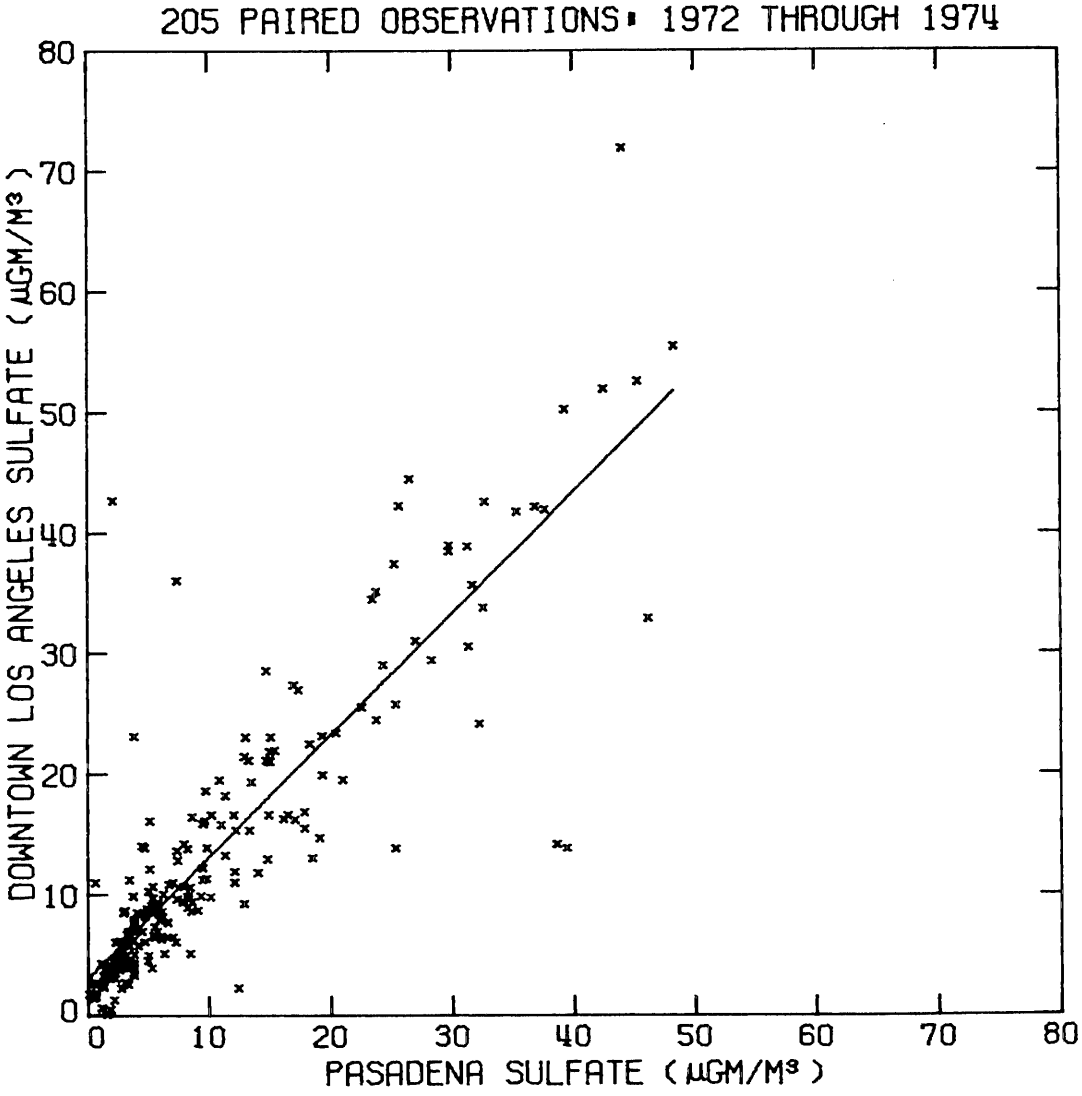
205 PAIRED OBSERVATIONS, 1972 THROUGH 1974
DOWNTOWN LOS ANGELES SULFATE (µGM/M³)
PASADENA SULFATE (µGM/M³)
0
10
20
30
40
50
60
70
80

FIGURE 2.11

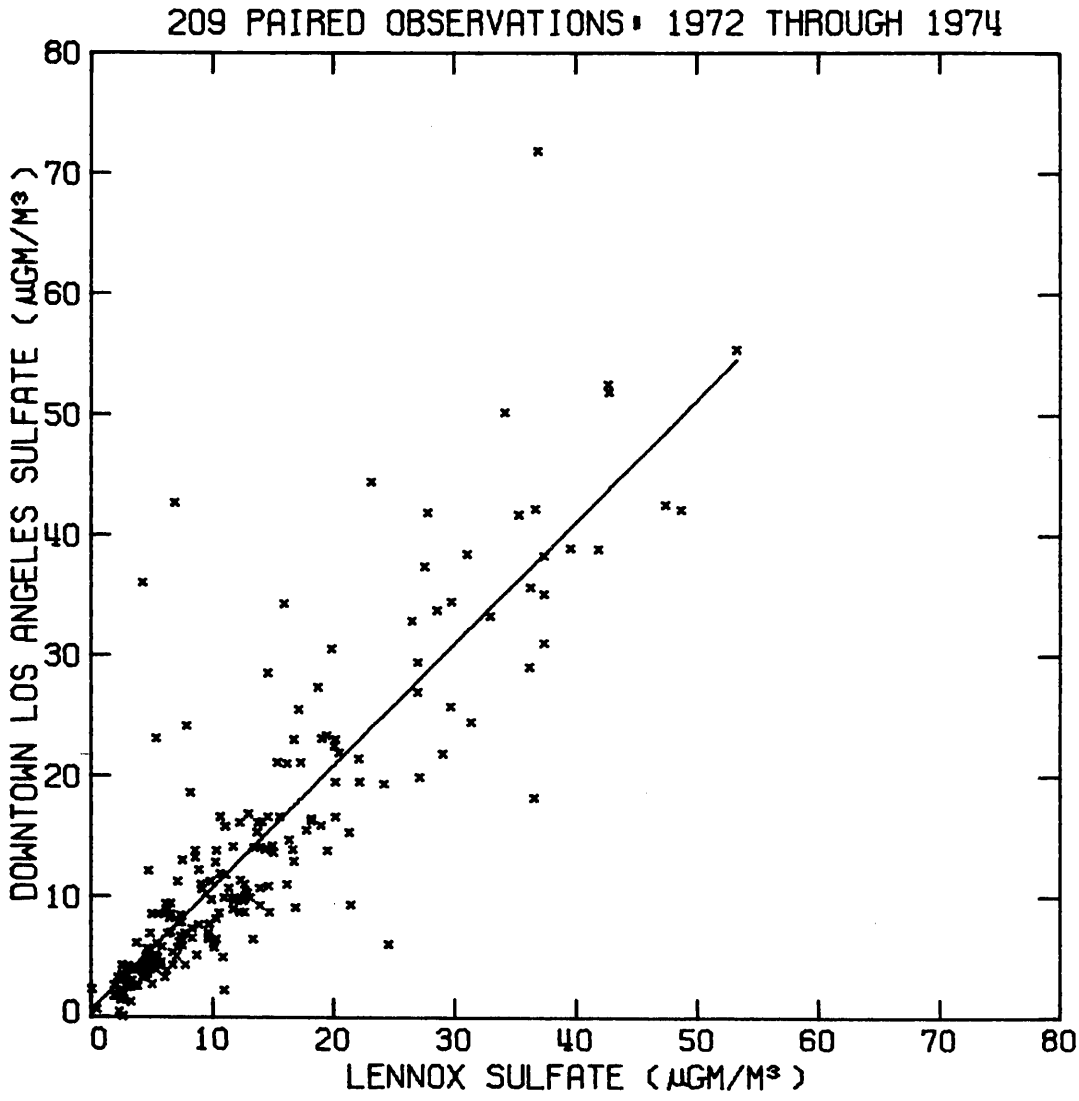
209 PAIRED OBSERVATIONS: 1972 THROUGH 1974
DOWNTOWN LOS ANGELES SULFATE (µGM/M³)
LENNOX SULFATE (µGM/M³)
0
10
20
30
40
50
60
70
80

FIGURE 2.12

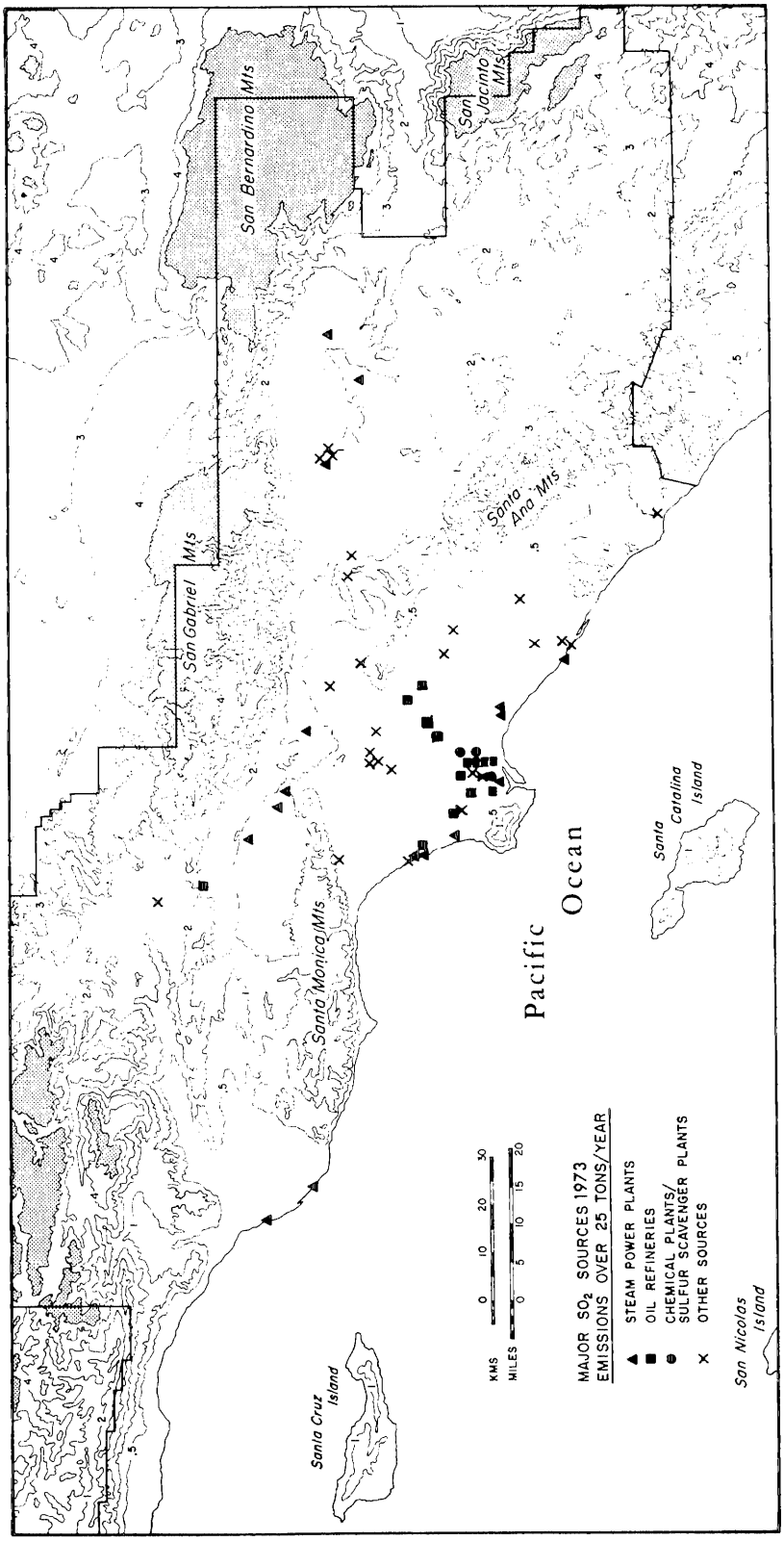
San Bernardino Mts
San Jacinto Mts
San Gabriel Mts
Santa Ana Mts
Santa Monica Mts
Pacific Ocean
Santa Catalina Island
Santa Cruz Island
San Nicolas Island
KMS 0 10 20 30
MILES 0 5 10 15 20
MAJOR SO2 SOURCES 1973
EMISSIONS OVER 25 TONS/YEAR
STEAM POWER PLANTS
OIL REFINERIES
CHEMICAL PLANTS/ SULFUR SCAVENGER PLANTS
OTHER SOURCES

FIGURE 2.13

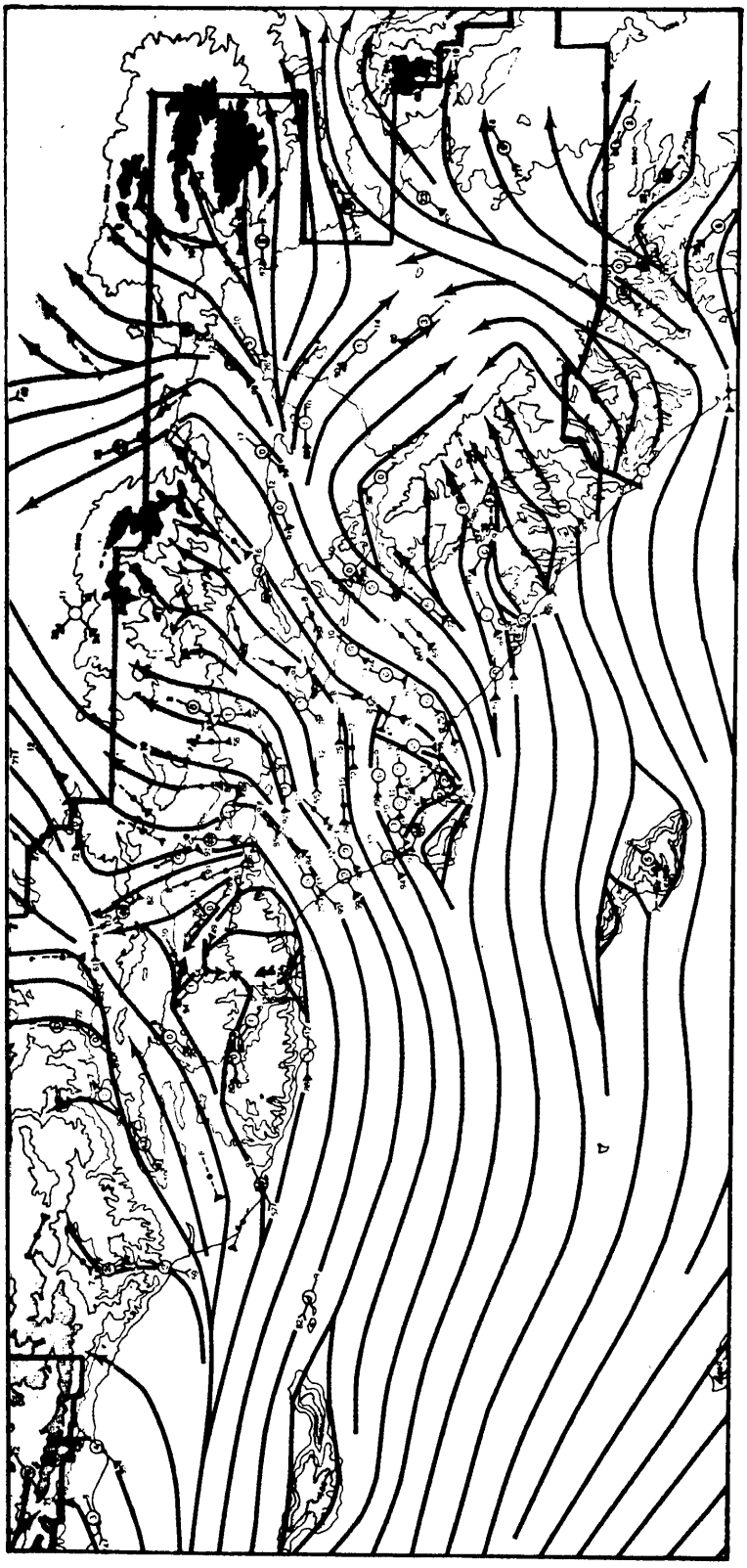

FIGURE 2.14

Typical Onshore Wind Flow Pattern
July 12:00-18:00 Hours PST
(From DeMarrais, Holzworth, and Hosler, 1965)

TABLE 2.4

Correlation Between Logs of Sulfate Observations at Pairs of Monitoring Stations: 1972-1974

		INLAND - WEST		LOS ANGELES COUNTY - COASTAL					LOS ANGELES COUNTY - CENTRAL								ORANGE COUNTY			EASTERN SAN GABRIEL VALLEY				EASTERN INLAND COUNTIES		ADJACENT BASINS
		THOUSAND OAKS	RESEDA	SANTA MONICA	WEST LA	LENNOX	TORRANCE	LONG BEACH	LYNWOOD	BURBANK	GLENDALE	LOS ANGELES	LOS ANGELES	PASADENA	PASADENA	GARDEN GROVE	ANAHEIM	ANAHEIM	SANTA ANA	AZUSA	WEST COVINA	GLENDORA	ONTARIO	RIVER-SIDE	SAN B'DINO	VISTA
		CHESS	LAAPCD	CHESS	LAAPCD	LAAPCD	NASN	NASN	LAAPCD	NASN	NASN	NASN	LAAPCD	LAAPCD	NASN	CHESS	CHESS	NASN	NASN	LAAPCD	CHESS	CHESS	NASN	NASN	NASN	CHESS
THOUSAND OAKS	CHESS	1.00	0.81	0.80	0.79	0.74	0.61	0.67	0.70	0.71	0.66	0.76	0.80	0.80	0.79	0.66	0.65	0.50	0.62	0.84	0.73	0.77	0.48	0.27	0.74	0.61
RESEDA	LAAPCD	0.81	1.00	0.68	0.80	0.74	0.46	0.20	0.73	0.69	0.69	0.62	0.78	0.82	0.44	0.60	0.61	0.03	0.33	0.86	0.74	0.77	0.41	0.51	0.60	0.51
SANTA MONICA	CHESS	0.80	0.68	1.00	0.80	0.82	0.65	0.75	0.85	0.78	0.62	0.77	0.78	0.76	0.72	0.71	0.73	0.63	0.65	0.78	0.76	0.75	0.41	0.27	0.73	0.68
WEST LA	LAAPCD	0.79	0.80	0.80	1.00	0.88	0.70	0.50	0.82	0.65	0.67	0.58	0.90	0.82	0.63	0.66	0.67	0.50	0.57	0.87	0.73	0.72	0.04	0.75	0.51	0.58
LENNOX	LAAPCD	0.74	0.74	0.82	0.88	1.00	0.54	0.68	0.90	0.67	0.79	0.50	0.86	0.84	0.70	0.77	0.74	0.58	0.76	0.83	0.74	0.76	0.07	0.92	0.62	0.68
TORRANCE	NASN	0.61	0.46	0.65	0.70	0.54	1.00	0.63	0.50	0.64	0.72	0.63	0.54	0.24	0.66	0.57	0.61	0.63	0.62	0.56	0.58	0.62	0.49	0.13	0.69	0.46
LONG BEACH	NASN	0.67	0.20	0.75	0.50	0.68	0.63	1.00	0.93	0.80	0.71	0.77	0.86	0.78	0.82	0.72	0.78	0.88	0.91	0.74	0.77	0.74	0.51	-0.11	0.74	0.66
LYNWOOD	LAAPCD	0.70	0.73	0.85	0.82	0.90	0.50	0.93	1.00	0.94	1.00	0.59	0.81	0.74	0.76	0.71	0.73	0.91	0.84	0.77	0.72	0.74	1.00	*	0.65	0.50
BURBANK	NASN	0.71	0.69	0.78	0.65	0.67	0.64	0.80	0.94	1.00	0.76	0.72	0.69	0.78	0.87	0.57	0.67	0.68	0.71	0.78	0.60	0.72	0.50	-0.12	0.77	0.53
GLENDALE	NASN	0.66	0.69	0.62	0.67	0.79	0.72	0.71	1.00	0.76	1.00	0.62	0.74	0.74	0.84	0.53	0.52	0.61	0.73	0.65	0.59	0.65	0.54	0.58	0.81	0.40
LOS ANGELES	NASN	0.76	0.62	0.77	0.58	0.50	0.63	0.77	0.59	0.72	0.62	1.00	0.63	0.57	0.71	0.58	0.68	0.70	0.72	0.54	0.73	0.67	0.27	0.50	0.70	0.44
LOS ANGELES	LAAPCD	0.80	0.78	0.78	0.90	0.86	0.54	0.86	0.81	0.69	0.74	0.63	1.00	0.85	0.80	0.75	0.75	0.67	0.86	0.89	0.71	0.76	0.25	0.71	0.65	0.67
PASADENA	LAAPCD	0.80	0.82	0.76	0.82	0.84	0.24	0.78	0.74	0.78	0.74	0.57	0.85	1.00	0.80	0.71	0.71	0.68	0.86	0.91	0.77	0.80	0.19	0.62	0.82	0.63
PASADENA	NASN	0.79	0.44	0.72	0.63	0.70	0.66	0.82	0.76	0.87	0.84	0.71	0.80	0.80	1.00	0.60	0.64	0.71	0.73	0.79	0.74	0.75	0.65	0.53	0.86	0.54
GARDEN GROVE	CHESS	0.66	0.60	0.71	0.66	0.77	0.57	0.72	0.71	0.57	0.53	0.58	0.75	0.71	0.60	1.00	0.86	0.64	0.74	0.74	0.75	0.74	0.37	0.62	0.64	0.73
ANAHEIM	CHESS	0.65	0.61	0.73	0.67	0.74	0.61	0.78	0.73	0.67	0.52	0.68	0.75	0.71	0.64	0.86	1.00	0.74	0.79	0.73	0.75	0.74	0.46	0.57	0.75	0.73
ANAHEIM	NASN	0.50	0.03	0.63	0.50	0.58	0.63	0.88	0.91	0.68	0.61	0.70	0.67	0.68	0.71	0.64	0.74	1.00	0.90	0.72	0.64	0.67	0.32	0.39	0.81	0.62
SANTA ANA	NASN	0.62	0.33	0.65	0.57	0.76	0.62	0.91	0.84	0.71	0.73	0.72	0.86	0.86	0.73	0.74	0.79	0.90	1.00	0.84	0.74	0.75	0.47	-0.10	0.73	0.71
AZUSA	LAAPCD	0.84	0.86	0.78	0.87	0.83	0.56	0.74	0.77	0.78	0.65	0.54	0.89	0.91	0.79	0.74	0.73	0.72	0.84	1.00	0.80	0.83	0.12	0.67	0.81	0.63
WEST COVINA	CHESS	0.73	0.74	0.76	0.73	0.74	0.58	0.77	0.72	0.60	0.59	0.73	0.71	0.77	0.74	0.75	0.75	0.64	0.74	0.80	1.00	0.87	0.44	0.49	0.77	0.68
GLENDORA	CHESS	0.77	0.77	0.75	0.72	0.76	0.62	0.74	0.74	0.72	0.65	0.67	0.76	0.80	0.75	0.74	0.74	0.67	0.75	0.83	0.87	1.00	0.47	0.29	0.82	0.67
ONTARIO	NASN	0.48	0.41	0.41	0.04	0.07	0.49	0.51	1.00	0.50	0.54	0.27	0.25	0.19	0.65	0.37	0.46	0.32	0.47	0.12	0.44	0.47	1.00	-0.08	0.67	0.50
RIVERSIDE	NASN	0.27	0.51	0.27	0.75	0.92	0.13	-0.11	*	-0.12	0.58	0.50	0.71	0.62	0.53	0.62	0.57	0.39	-0.10	0.67	0.49	0.29	-0.08	1.00	0.54	0.33
SAN BERNARDINO	NASN	0.74	0.60	0.73	0.51	0.62	0.69	0.74	0.65	0.77	0.81	0.70	0.65	0.82	0.86	0.64	0.75	0.81	0.73	0.81	0.77	0.82	0.67	0.54	1.00	0.64
VISTA	CHESS	0.61	0.51	0.68	0.58	0.66	0.46	0.66	0.50	0.53	0.40	0.44	0.67	0.63	0.54	0.73	0.73	0.62	0.71	0.63	0.68	0.67	0.50	0.33	0.64	1.00

Sulfate observations below 2 $\mu gm/m^3$ disregarded.

TABLE 2.5

Number of Paired Observations with Sulfate Concentration Greater Than or Equal to 2 μgm/m^3: 1972-1974

		INLAND - WEST		LOS ANGELES COUNTY - COASTAL					LOS ANGELES COUNTY - CENTRAL							ORANGE COUNTY				EASTERN SAN GABRIEL VALLEY				EASTERN INLAND COUNTIES		ADJACENT BASINS
		THOUSAND OAKS CHESS	RESEDA LAAPCD	SANTA MONICA CHESS	WEST LA LAAPCD	LENNOX LAAPCD	TORRANCE NASN	LONG BEACH NASN	LYNWOOD LAAPCD	BURBANK NASN	GLENDALE NASN	LOS ANGELES NASN	LOS ANGELES LAAPCD	PASADENA LAAPCD	PASADENA NASN	GARDEN GROVE CHESS	ANAHEIM CHESS	ANAHEIM NASN	SANTA ANA NASN	AZUSA LAAPCD	WEST COVINA CHESS	GLENDORA CHESS	ONTARIO NASN	RIVERSIDE NASN	SAN B'DINO NASN	VISTA CHESS
THOUSAND OAKS	CHESS	765.	141.	671.	141.	150.	58.	59.	48.	68.	52.	56.	147.	140.	57.	698.	683.	58.	58.	140.	684.	646.	43.	11.	51.	705.
RESEDA	LAAPCD	141.	192.	143.	182.	191.	14.	14.	53.	14.	11.	11.	181.	180.	14.	152.	167.	16.	14.	178.	154.	155.	12.	4.	13.	174.
SANTA MONICA	CHESS	671.	143.	800.	146.	159.	61.	57.	45.	67.	52.	60.	154.	141.	56.	733.	728.	59.	61.	141.	747.	710.	43.	11.	51.	727.
WEST LA	LAAPCD	141.	182.	146.	194.	193.	15.	15.	57.	15.	12.	12.	185.	182.	15.	157.	168.	17.	15.	182.	158.	157.	12.	4.	13.	177.
LENNOX	LAAPCD	150.	191.	159.	193.	217.	15.	16.	63.	16.	14.	13.	199.	191.	16.	172.	185.	18.	16.	192.	167.	172.	13.	4.	14.	191.
TORRANCE	NASN	58.	14.	61.	15.	15.	83.	60.	5.	61.	39.	55.	15.	12.	53.	63.	73.	66.	70.	14.	61.	65.	47.	8.	59.	77.
LONG BEACH	NASN	59.	14.	57.	15.	16.	60.	79.	6.	63.	43.	55.	16.	13.	56.	60.	69.	64.	67.	15.	59.	61.	48.	10.	53.	73.
LYNWOOD	LAAPCD	48.	53.	45.	57.	63.	5.	6.	63.	5.	2.	3.	59.	52.	5.	54.	50.	6.	6.	54.	52.	45.	2.	0.	4.	60.
BURBANK	NASN	68.	14.	67.	15.	16.	61.	63.	5.	90.	43.	64.	16.	14.	57.	70.	80.	66.	67.	15.	67.	74.	51.	8.	61.	81.
GLENDALE	NASN	52.	11.	52.	12.	14.	39.	43.	2.	43.	69.	42.	14.	10.	40.	56.	61.	45.	45.	13.	52.	55.	38.	8.	42.	63.
LOS ANGELES	NASN	56.	11.	60.	12.	13.	55.	55.	3.	64.	42.	82.	13.	11.	51.	61.	74.	65.	62.	13.	60.	66.	46.	9.	58.	74.
LOS ANGELES	LAAPCD	147.	181.	154.	185.	199.	15.	16.	59.	16.	14.	13.	203.	183.	16.	164.	177.	18.	16.	185.	163.	163.	13.	4.	14.	182.
PASADENA	LAAPCD	140.	180.	141.	182.	191.	12.	13.	52.	14.	10.	11.	183.	192.	12.	153.	166.	14.	12.	184.	152.	156.	12.	4.	13.	173.
PASADENA	NASN	57.	14.	56.	15.	16.	53.	56.	5.	57.	40.	51.	16.	12.	79.	60.	70.	59.	59.	15.	58.	63.	43.	6.	50.	72.
GARDEN GROVE	CHESS	698.	152.	733.	157.	172.	63.	60.	54.	70.	56.	61.	164.	153.	60.	854.	744.	62.	64.	153.	750.	698.	47.	11.	57.	769.
ANAHEIM	CHESS	683.	167.	728.	168.	185.	73.	69.	50.	80.	61.	74.	177.	166.	70.	744.	906.	73.	74.	168.	739.	785.	55.	15.	64.	834.
ANAHEIM	NASN	58.	16.	59.	17.	18.	66.	64.	6.	66.	45.	65.	18.	14.	59.	62.	73.	82.	72.	17.	58.	65.	54.	9.	64.	74.
SANTA ANA	NASN	58.	14.	61.	15.	16.	70.	67.	6.	67.	45.	62.	16.	12.	59.	64.	74.	72.	83.	15.	61.	66.	52.	10.	62.	77.
AZUSA	LAAPCD	140.	178.	141.	182.	192.	14.	15.	54.	15.	13.	13.	185.	184.	15.	153.	168.	17.	15.	193.	154.	156.	13.	4.	13.	174.
WEST COVINA	CHESS	684.	154.	747.	158.	167.	61.	59.	52.	67.	52.	60.	163.	152.	58.	750.	739.	68.	61.	154.	826.	733.	41.	11.	51.	763.
GLENDORA	CHESS	646.	155.	710.	157.	172.	65.	61.	45.	74.	55.	66.	163.	156.	63.	698.	785.	65.	66.	156.	733.	859.	47.	13.	60.	795.
ONTARIO	NASN	43.	12.	43.	12.	13.	47.	48.	2.	51.	38.	46.	13.	12.	43.	47.	55.	54.	52.	13.	41.	47.	63.	10.	48.	56.
RIVERSIDE	NASN	11.	4.	11.	4.	4.	8.	10.	0.	8.	8.	9.	4.	4.	6.	11.	15.	9.	10.	4.	11.	13.	10.	17.	10.	16.
SAN BERNARDINO	NASN	51.	13.	51.	13.	14.	59.	53.	4.	61.	42.	58.	14.	13.	50.	57.	64.	64.	62.	13.	51.	60.	48.	10.	74.	68.
VISTA	CHESS	705.	174.	727.	177.	191.	77.	73.	60.	81.	63.	74.	182.	173.	72.	769.	834.	74.	77.	174.	763.	795.	56.	16.	68.	955.

from which to compute each correlation coefficient. For reasons explained previously, only those sulfate observations reported at or above 2 $\mu gm/m^3$ were considered.

Measurements taken on the same day at all of the LAAPCD stations are highly correlated (about 0.80 to 0.90) with each other. The correlation between pairs of CHESS stations is typically in the range of 0.80 to 0.70. The log-linear correlations between pairs of NASN stations typically lie in the range 0.80 to 0.60. The NASN station at Ontario, however, provides an exception to this pattern: it does not correlate well with observations at other monitoring sites. The distribution of correlation coefficients between station pairs involving more than one monitoring agency is similar to the distribution of correlation coefficients between pairs of stations operated solely by NASN. The distribution of correlation coefficients between monitoring programs is summarized in Table 2.6.

Examination of Table 2.4 shows that most of the highest correlation coefficients (above 0.80) involve pairings with LAAPCD stations. But if one examines the variance of the logs of the sulfate observations, β^2, in Table 2.3, they will note that it is data from the LAAPCD network that deviate most noticeably from long-run distributional equivalence with data from neighboring stations operated by other monitoring agencies. In contrast, the NASN and CHESS air monitoring results show more consistent statistical distributions, but lower cross-correlation between simultaneous individual samples. The explanation for that behavior is probably found in mismatches between the sampling schedules

TABLE 2.6

DISTRIBUTION OF CORRELATION COEFFICIENTS: 1972 through 1974

Correlation Coefficients taken from Table 2.4

Correlation Between Logs of Simultaneous Observations	Number of Station Pairs Whose Cross Correlation Falls in the Range Stated:			
	Station Pairs within the Same Monitoring Program			Station Pairs in Two Different Monitoring Programs
	CHESS	LAAPCD	NASN	
1.00 to 0.90		3	2	4
0.89 to 0.80	3	13	8	20
0.79 to 0.70	12	5	16	66
0.69 to 0.60	6		12	53
0.59 to 0.50			7	28
0.49 to 0.40			2	12
0.39 to 0.30			2	3
0.29 to 0.20			1	6
0.19 to 0.10			1	2
0.09 to 0.00			0	3
-0.10 to -0.01			2	
-0.20 to -0.11			2	
Insufficient Data				3

maintained by different agencies as described in Appendix B1. The CHESS sampling period, for example, is offset by about a half day from that of the NASN and APCD samples reported for the same "day". Sample start and stop times may have differed at stations within the CHESS network itself. This cannot help but reduce the day-to-day correlation between CHESS and other agencies' data since fully comparable "events" have not been sampled. In the case of the NASN data, a review of the reported dates on which sulfate samples were taken indicates that the NASN volunteer operators often run their samples on days other than those assigned, especially when assigned days fall on a weekend. There is some doubt as to the exact date on which some of the NASN data were actually collected. In both of these instances, a mismatch in sampling schedules between monitoring agencies would reduce the apparent day-to-day correlation between stations. The long-run statistics and distribution of the data collected would be unaffected since all samples taken at a station would still be drawn from the underlying population of events at that location even if the information on the date of a given event was confused somewhat. Correlation coefficients given in Table 2.4 thus probably understate the true degree to which 24-hour average sulfate concentrations tracked each other at pairs of monitoring sites during the three years of interest.

Widespread similarity in seasonal sulfate concentration trends and a high positive correlation between samples taken on the same day at widely separated air monitoring stations leads to two more important physical generalizations.

Generalization 4: Major sulfate concentration trends appear to be determined by forcing functions which are felt over the entire South Coast Air Basin.

Generalization 5: Sulfate concentration changes are felt to a large degree on a basin-wide basis within the same 24-hour period.

This suggests that mesoscale and larger meteorological fluctuations may be the dominant determinants of sulfate concentration changes from day-to-day within this particular airshed. An extremely detailed *spatial* representation of meteorological inputs and chemical mechanisms within our air quality model might be unnecessary. A relatively uncomplicated emissions to air quality model should be attempted initially to test its explanatory power.

2.2.7 Selection of an Averaging Time for Air Quality Model Calculations

It is clear from Figures 2.4, 2.8, 2.9 and 2.10 that temporal trends in sulfate air quality are more pronounced than average spatial gradients. Thus for an air quality model to verify its explanatory power, relatively short time averaging of concentration predictions would be desired. The implications of averaging sulfate concentrations over shorter time intervals within our three year study period will be explored.

Tables 2.7, 2.8 and 2.9 present the results of the statistical methods of Appendix B4 applied separately to data from the years 1972, 1973 and 1974. As the number of samples being considered within a group declines, the confidence interval associated with the group mean

TABLE 2.7

Statistical Description of Sulfate Air Quality Data in the South Coast Air Basin: 1972

		ARITHMETIC STATISTICS					GEOMETRIC STATISTICS				
		SAMPLE ARITHMETIC MEAN $\bar{y}$	SAMPLE ARITHMETIC STANDARD DEVIATION σ	NUMBER OF SAMPLES n	LOWER CONFIDENCE LIMIT ON $\bar{y}$ (2.5 %ile)	UPPER CONFIDENCE LIMIT ON $\bar{y}$ (97.5 %ile)	ESTIMATED MEAN LOG α	ESTIMATED VARIANCE OF LOGS β^2	ESTIMATED GEOMETRIC MEAN μ_g	ESTIMATED GEOMETRIC STANDARD DEVIATION σ_g	ARITHMETIC MEAN ESTIMATED FROM α and β^2
THOUSAND OAKS	CHESS	8.25	7.31	231.00	7.61	8.89	1.88	0.48	6.58	2.00	8.38
RESEDA	LAAPCD	15.99	15.75	72.00	12.71	19.26	2.37	0.82	10.65	2.47	16.05
SANTA MONICA	CHESS	9.40	5.84	238.00	8.87	9.92	2.09	0.32	8.05	1.76	9.44
WEST LA	LAAPCD	11.86	9.04	72.00	9.98	13.74	2.23	0.48	9.32	1.99	11.83
LENNOX	LAAPCD	15.37	9.78	73.00	13.35	17.39	2.56	0.33	13.00	1.77	15.31
TORRANCE	NASN	11.34	6.35	30.00	9.15	13.52	2.30	0.26	9.96	1.66	11.32
LONG BEACH	NASN	11.29	7.55	29.00	9.59	13.98	2.27	0.30	9.63	1.73	11.19
LYNWOOD	LAAPCD	*	*	0.0	*	*	*	*	*	*	*
BURBANK	NASN	11.18	7.87	29.00	8.42	13.94	2.18	0.52	8.85	2.06	11.50
GLENDALE	NASN	10.27	7.27	28.00	7.68	12.87	2.12	0.44	8.35	1.94	10.40
LOS ANGELES	NASN	11.07	8.19	32.00	8.35	13.79	2.22	0.35	9.16	1.81	10.91
LOS ANGELES	LAAPCD	14.38	11.60	68.00	11.88	16.88	2.41	0.48	11.17	2.00	14.19
PASADENA	LAAPCD	11.55	10.77	70.00	9.27	13.82	2.12	0.62	8.29	2.19	11.29
PASADENA	NASN	10.67	7.58	27.00	7.91	13.43	2.13	0.53	8.39	2.08	10.96
GARDEN GROVE	CHESS	9.20	5.39	239.00	8.72	9.69	2.08	0.33	8.01	1.78	9.47
ANAHEIM	CHESS	10.95	7.68	328.00	10.52	11.39	2.21	0.38	9.15	1.85	11.07
ANAHEIM	NASN	11.19	8.24	28.00	8.25	14.13	2.19	0.50	8.91	2.03	11.46
SANTA ANA	NASN	11.69	11.06	29.00	7.82	15.56	2.20	0.46	9.06	1.97	11.40
AZUSA	LAAPCD	13.98	11.91	71.00	11.48	16.48	2.33	0.63	10.30	2.21	14.12
WEST COVINA	CHESS	11.06	6.77	241.00	10.46	11.66	2.23	0.38	9.30	1.85	11.25
GLENDORA	CHESS	11.98	9.63	303.00	11.38	12.58	2.22	0.57	9.19	2.13	12.24
ONTARIO	NASN	10.03	8.29	28.00	7.87	12.99	2.01	0.55	7.43	2.16	9.99
RIVERSIDE	NASN	11.40	6.54	18.00	8.44	14.36	2.29	0.33	9.92	1.78	11.70
SAN BERNARDINO	NASN	11.06	7.90	30.00	8.34	13.78	2.15	0.59	8.57	2.16	11.52
VISTA	CHESS	9.66	6.82	336.00	9.29	10.03	2.09	0.36	8.07	1.83	9.67

AN ASTERISK (*) INDICATES DATA THAT ARE UNAVAILABLE

TABLE 2.8

Statistical Description of Sulfate Air Quality Data in the South Coast Air Basin: 1973

		ARITHMETIC STATISTICS					GEOMETRIC STATISTICS				
		SAMPLE ARITHMETIC MEAN $\bar{y}$	SAMPLE ARITHMETIC STANDARD DEVIATION σ	NUMBER OF SAMPLES n	LOWER CONFIDENCE LIMIT ON $\bar{y}$ (2.5 %ile)	UPPER CONFIDENCE LIMIT ON $\bar{y}$ (97.5 %ile)	ESTIMATED MEAN LOG α	ESTIMATED VARIANCE OF LOGS β^2	ESTIMATED GEOMETRIC MEAN ν_g	ESTIMATED GEOMETRIC STANDARD DEVIATION σ_g	ARITHMETIC MEAN ESTIMATED FROM α and β^2
THOUSAND OAKS	CHESS	11.03	10.96	352.00	10.58	11.49	1.95	1.02	7.06	2.75	11.77
RESEDA	LAAPCD	16.45	21.17	72.00	12.05	20.84	2.03	1.77	7.65	3.78	18.50
SANTA MONICA	CHESS	12.49	10.10	354.00	12.04	12.94	2.23	0.64	9.33	2.23	12.86
WEST LA	LAAPCD	10.63	10.47	71.00	8.44	12.83	1.89	1.05	6.59	2.79	11.14
LENNOX	LAAPCD	13.94	12.17	73.00	11.43	16.45	2.28	0.77	9.73	2.41	14.33
TORRANCE	NASN	11.21	7.43	25.00	8.39	14.03	2.23	0.38	9.32	1.86	11.28
LONG BEACH	NASN	10.59	5.58	25.00	8.47	12.70	2.25	0.21	9.50	1.58	10.54
LYNWOOD	LAAPCD	*	*	0.0	*	*	*	*	*	*	*
BURBANK	NASN	14.87	11.32	31.00	11.05	18.70	2.45	0.54	11.55	2.08	15.12
GLENDALE	NASN	10.46	7.82	30.00	7.77	13.15	2.14	0.41	8.47	1.90	10.42
LOS ANGELES	NASN	12.30	6.59	25.00	9.80	14.80	2.37	0.29	10.71	1.71	12.35
LOS ANGELES	LAAPCD	15.80	14.70	73.00	12.77	18.83	2.35	0.91	10.51	2.59	16.55
PASADENA	LAAPCD	12.66	12.33	73.00	10.12	15.20	2.02	1.15	7.56	2.93	13.47
PASADENA	NASN	13.59	9.93	30.00	10.18	17.00	2.36	0.55	10.63	2.10	14.00
GARDEN GROVE	CHESS	13.23	8.76	352.00	12.79	13.67	2.36	0.50	10.57	2.03	13.57
ANAHEIM	CHESS	12.31	9.18	352.00	11.88	12.75	2.25	0.62	9.44	2.20	12.89
ANAHEIM	NASN	9.48	5.40	25.00	7.43	11.54	2.09	0.33	8.12	1.78	9.60
SANTA ANA	NASN	8.02	3.64	25.00	6.64	9.41	1.99	0.19	7.31	1.56	8.06
AZUSA	LAAPCD	13.11	11.98	73.00	10.64	15.58	2.10	1.10	8.18	2.86	14.19
WEST COVINA	CHESS	14.54	12.00	347.00	13.98	15.09	2.29	0.90	9.91	2.58	15.55
GLENDORA	CHESS	14.43	12.10	356.00	13.91	14.95	2.28	0.91	9.77	2.59	15.40
ONTARIO	NASN	10.50	7.10	21.00	7.55	13.45	2.16	0.39	8.71	1.87	10.59
RIVERSIDE	NASN	*	*	0.0	*	*	*	*	*	*	*
SAN BERNARDINO	NASN	15.69	14.34	22.00	9.87	21.51	2.42	0.71	11.24	2.32	16.00
VISTA	CHESS	10.03	7.58	350.00	9.67	10.39	2.02	0.66	7.51	2.25	10.43

AN ASTERISK (*) INDICATES DATA THAT ARE UNAVAILABLE

TABLE 2.9

Statistical Description of Sulfate Air Quality Data in the South Coast Air Basin: 1974

		ARITHMETIC STATISTICS					GEOMETRIC STATISTICS				
		SAMPLE ARITHMETIC MEAN $\bar{y}$	SAMPLE ARITHMETIC STANDARD DEVIATION σ	NUMBER OF SAMPLES n	LOWER CONFIDENCE LIMIT ON $\bar{y}$ (2.5 %ile)	UPPER CONFIDENCE LIMIT ON $\bar{y}$ (97.5 %ile)	ESTIMATED MEAN LOG α	ESTIMATED VARIANCE OF LOGS β^2	ESTIMATED GEOMETRIC MEAN μ_g	ESTIMATED GEOMETRIC STANDARD DEVIATION σ_g	ARITHMETIC MEAN ESTIMATED FROM α and β^2
THOUSAND OAKS	CHESS	8.42	7.54	307.00	7.97	8.86	1.77	0.81	5.86	2.46	8.80
RESEDA	LAAPCD	11.05	10.72	70.00	8.78	13.32	1.86	1.29	6.41	3.11	12.20
SANTA MONICA	CHESS	11.32	8.95	248.00	10.59	12.05	2.12	0.67	8.33	2.27	11.67
WEST LA	LAAPCD	9.42	8.92	72.00	7.57	11.28	1.76	1.09	5.81	2.85	10.03
LENNOX	LAAPCD	11.82	10.01	73.00	9.76	13.89	2.13	0.71	8.38	2.32	11.93
TORRANCE	NASN	11.65	6.29	28.00	9.40	13.89	2.32	0.28	10.21	1.70	11.75
LONG BEACH	NASN	13.95	9.21	26.00	10.53	17.37	2.48	0.30	11.89	1.73	13.81
LYNWOOD	LAAPCD	9.47	8.55	68.00	7.63	11.31	1.87	0.81	6.46	2.46	9.70
BURBANK	NASN	18.02	29.20	30.00	7.98	28.05	2.47	0.45	11.81	1.96	14.83
GLENDALE	NASN	9.02	8.80	13.00	4.31	13.72	1.89	0.63	6.64	2.22	9.12
LOS ANGELES	NASN	13.92	12.09	26.00	9.43	18.41	2.30	0.75	9.95	2.38	14.47
LOS ANGELES	LAAPCD	12.66	11.19	71.00	10.31	15.00	2.10	0.98	8.20	2.69	13.36
PASADENA	LAAPCD	8.56	8.41	71.00	6.80	10.32	1.67	1.11	5.31	2.87	9.24
PASADENA	NASN	11.47	9.23	22.00	7.72	15.22	2.22	0.39	9.24	1.87	11.26
GARDEN GROVE	CHESS	10.09	6.82	307.00	9.65	10.52	2.10	0.45	8.18	1.96	10.24
ANAHEIM	CHESS	10.69	7.89	286.00	10.15	11.24	2.12	0.52	8.36	2.06	10.87
ANAHEIM	NASN	12.51	9.10	30.00	9.38	15.63	2.31	0.44	10.09	1.95	12.60
SANTA ANA	NASN	11.47	7.48	29.00	8.85	14.09	2.27	0.34	9.65	1.79	11.44
AZUSA	LAAPCD	10.54	9.96	71.00	8.45	12.62	1.92	1.00	6.85	2.71	11.26
WEST COVINA	CHESS	11.49	9.00	293.00	10.90	12.09	2.14	0.66	8.53	2.26	11.89
GLENDORA	CHESS	11.13	9.08	278.00	10.49	11.77	2.08	0.73	8.02	2.35	11.58
ONTARIO	NASN	13.49	8.05	15.00	9.49	17.49	2.42	0.42	11.25	1.91	13.86
RIVERSIDE	NASN	*	*	0.0	*	*	*	*	*	*	*
SAN BERNARDINO	NASN	12.32	9.68	23.00	8.48	16.16	2.23	0.62	9.27	2.20	12.67
VISTA	CHESS	8.66	6.68	349.00	8.34	8.97	1.90	0.55	6.70	2.10	8.82

AN ASTERISK (*) INDICATES DATA THAT ARE UNAVAILABLE

value of course widens. When attention is turned to even shorter time periods, such as a month, the result is well illustrated by Figures 2.15 and 2.16. These figures show the monthly arithmetic means of all sulfate samples taken at typical CHESS and LAAPCD stations during the period 1972 through 1974. The o's indicate the magnitude of the monthly averages of the raw sulfate data, $\bar{y}$, while the +'s indicate an estimate of the arithmetic mean of the underlying population of events, μ, calculated from a log-normality assumption applied to those sulfate values above 2 $\mu gm/m^3$ by the methods outlined in Appendix B4. In general, correspondence between $\bar{y}$ and μ is still close, even for the LAAPCD stations which average only 6 samples per month. The important feature of these graphs, however, is that the 95% confidence intervals on the monthly means of the LAAPCD data have become quite large due to the small number of samples taken each month. The NASN data have not been plotted at all since the insufficiency of data is even more extreme (only one or two samples per month). A graphical description of the monthly arithmetic means of the CHESS and LAAPCD sulfate data at all monitoring stations is given at the end of Appendix B4.

These confidence interval estimates hold important implications for a long-term air quality modeling study. It is clear from the previous discussion plus Appendix B4 that rather long averaging times are needed to reduce the uncertainty introduced into the NASN and LAAPCD data averages by their sparse sampling schedules. A compromise must be struck between the desire for short averaging times and the

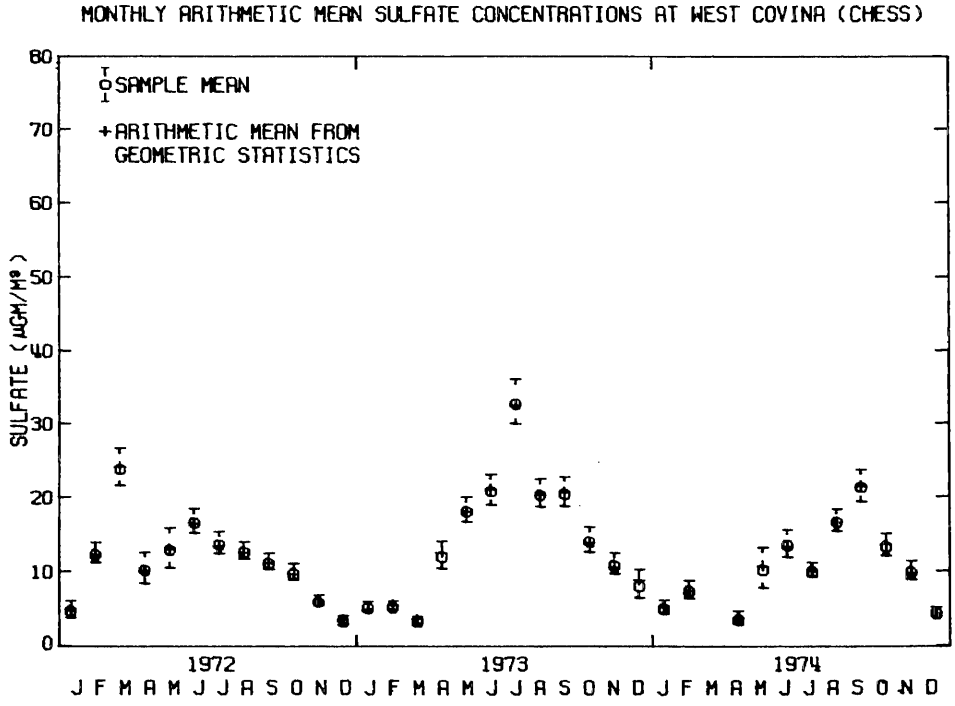

FIGURE 2.15

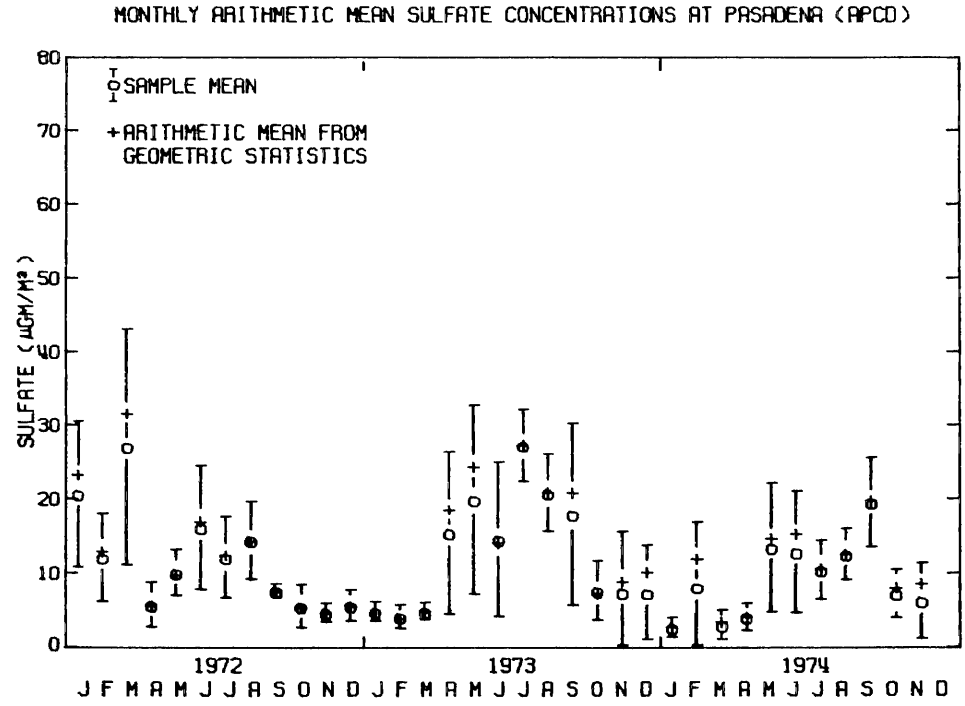

FIGURE 2.16

desire for tight confidence intervals on the ambient concentration averages used to validate air quality model predictions.

Monthly average sulfate concentrations will be modeled with the understanding that only the CHESS data and certain portions of the LAAPCD data strings will provide an exacting test of model performance on a monthly basis. These monthly predictions can then be combined to form annual average predictions for comparison to annual average air quality measurements which are known to $\pm$ a few micrograms per cubic meter at a larger number of monitoring sites.

2.3 Sulfate Air Quality in Relation to the Total Sulfur Content of the Atmosphere

The reason for the localized sulfate enrichment of the air over metropolitan Los Angeles is likely to be found in emissions of sulfur oxides from fuel burning and industrial activities. Roberts (1975) has outlined the atmospheric sulfur budget of the Los Angeles area, as shown in Figure 2.17. His calculations indicate that while only about thirty percent of the global sulfur emissions are due to man's activities, ninety-eight percent of the sulfur emissions within the Los Angeles Basin are attributable to man-made pollution sources. Most of these emissions are in the form of sulfur dioxide gas.

Sulfur dioxide emissions undergo transport, dilution, and removal processes in the atmosphere. Chemical reactions proceed which can oxidize sulfur dioxide gas to form particulate sulfates downwind from SO_2 emission sources. With the exception of trace amounts of other sulfur compounds, such as H_2S, sulfur dioxide and particulate

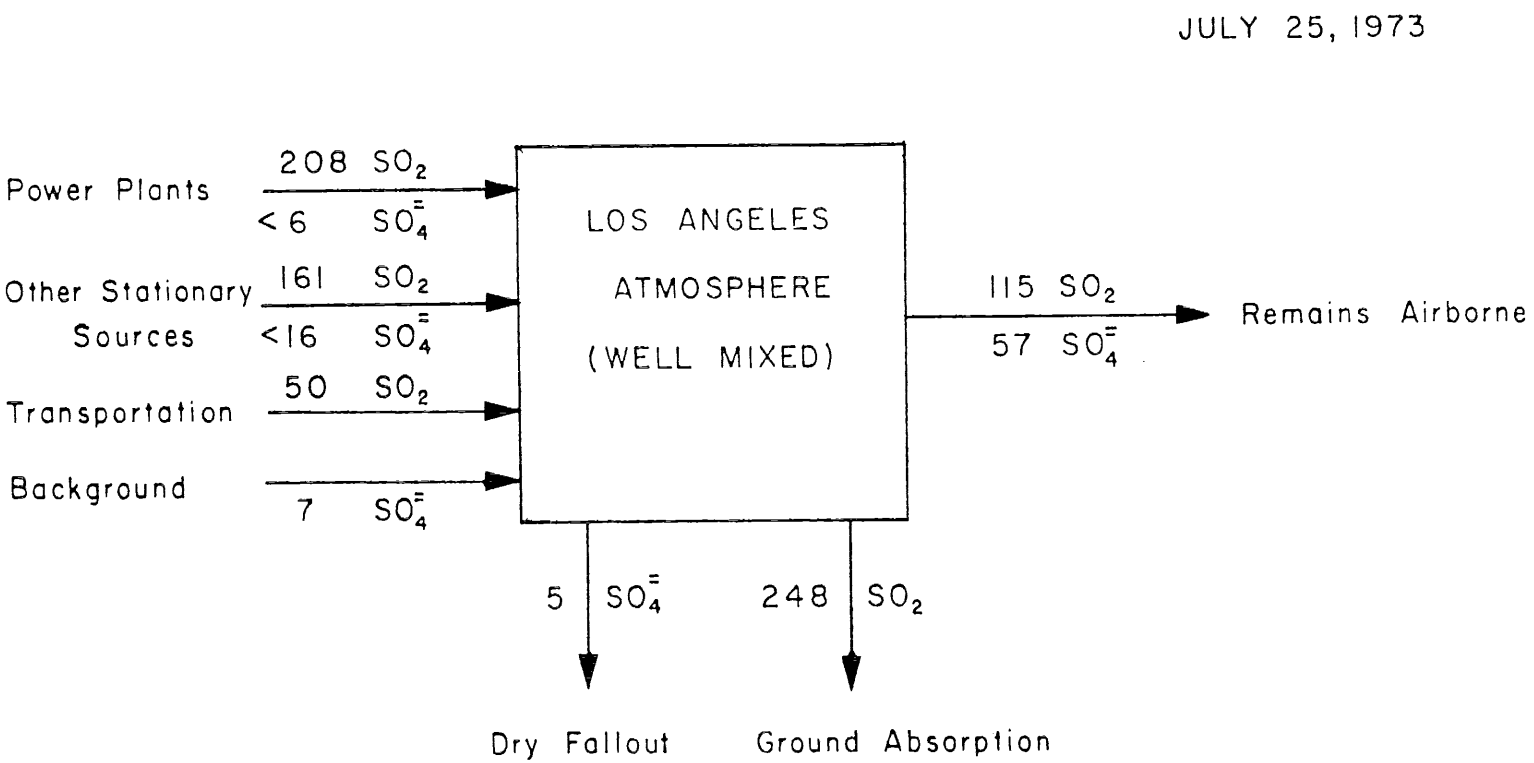

FIGURE 2.17

The Los Angeles Basin Atmospheric Sulfur Balance for July 25, 1973 (from Roberts 1975)

sulfur oxides (measured as sulfates) together make up the total sulfur burden of the Los Angeles area atmosphere. The atmospheric ratio of particulate sulfur to total sulfur, f_s, is a convenient indicator of the extent to which the reaction of SO_2 to form "sulfates" has reached completion. This ratio can be computed in the course of our air quality modeling study, and provides a check on the computed rate of removal of SO_2 from the gas phase.

Sulfur oxides emissions within the South Coast Air Basin are generated primarily by activities at power plants, oil refineries, chemical plants and metallurgical operations. Figure 2.13 shows the location of major sulfur oxides emission sources in that air basin. According to 1974 emission inventory information (Hunter and Helgeson, 1976), about eighty percent of the stationary source sulfur oxides emissions in the South Coast Air Basin originate from sources adjacent to the coast. Prevailing winds transport these coastal emissions inland along resultant sea-breeze wind trajectories as indicated in Figure 2.14, (De Marrais, Holzworth, and Hosler, 1965). At locations upwind or to the side of major SO_2 emission sources, a large percentage of the observed sulfate will be of the background variety, and the value of f_s could be relatively high. At distances close to major SO_2 emission sources, most of the sulfur in the atmosphere will appear as SO_2, and the value of f_s will be relatively low. Then at distances further downwind, conversion of SO_2 to form sulfates, plus removal of SO_2 at the earth's surface should act to raise the value of f_s. Let us

examine the available air quality data to see if these hypotheses are supported.

In the absence of direct air monitoring data for total sulfur, as would be revealed by a flame photometric total sulfur analyzer, a close approximation to f_s should be obtainable from:

$$f_s = \frac{S_p}{S_T} \approx \frac{S_{SO_4}}{S_{SO_2} + S_{SO_4}} \qquad (2.1)$$

where

S_p is particulate sulfur concentration.

S_T is total sulfur concentration.

S_{SO_4} is particulate sulfur oxides concentration measured as sulfates and restated in $\mu gm/m^3$ as elemental sulfur.

S_{SO_2} is sulfur dioxide concentration in $\mu gm/m^3$ as elemental sulfur.

Both S_p and S_T could be considered as air pollutants. If they were mutually independent and log-normally distributed, then f_s should also be log-normally distributed. Stochastic independence of S_p and S_T is rather doubtful, however, in light of the way in which they are estimated in equation (2.1). The distribution of f_s is therefore uncertain. In Figures 2.18, 2.19 and 2.20, the cumulative distribution of f_s is displayed for typical CHESS, NASN, and LAAPCD stations. Similar graphs for the remaining stations are presented in Appendix B6. The rapid fall-off at the lower tails of the CHESS and LAAPCD distributions again probably is due to the problems with measurement of very low sulfate concentrations. At the upper tails of the CHESS and NASN

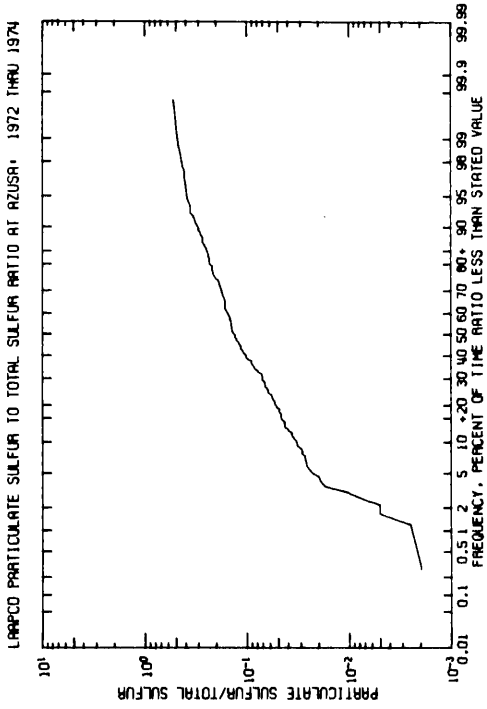

FIGURE 2.19

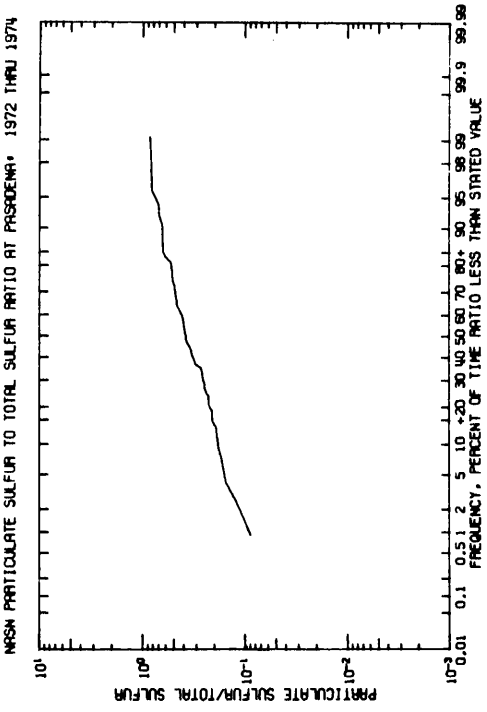

FIGURE 2.18

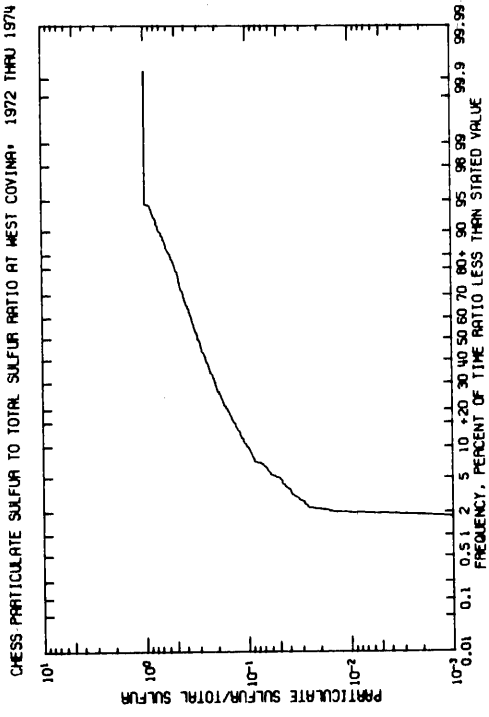

FIGURE 2.20

distributions, a flattening of the curve at $f_s = 1$ is caused by reported zero concentrations of sulfur dioxide.

In Table 2.10 the three year arithmetic mean values of f_s are shown, labeled by geographic location and monitoring agency. It is seen that the CHESS and NASN stations located in close proximity display roughly the same values of f_s, while values of f_s at the LAAPCD stations are systematically lower. We already know that the sulfate observations are not the cause of such large differences between monitoring agencies. Therefore, it follows that the lower values of f_s at the APCD stations are due to systematically higher SO_2 measurements as would be expected from the discussions in Appendix B1.

It is not possible on the basis of these differences alone to state that any particular SO_2 data base is "correct". A good case can be made for the assertion that the true SO_2 values should lie somewhere between the results obtained by the APCD's conductometric technique and the West-Gaeke technique employed by CHESS and NASN. The minimum detection limit of the LAAPCD SO_2 monitoring instruments is 26 $\mu gm/m^3$. All SO_2 concentrations below that value would also be reported as 26 $\mu gm/m^3$. The APCD instruments encounter SO_2 concentrations at or below their minimum detection limit much of the time. Twenty-four hour average SO_2 concentrations constructed from APCD data thus often will be biased high. In contrast CHESS and NASN data possibly underestimate SO_2 levels due to sample collection efficiency problems, and due to lack of control of the time-temperature history of samples

TABLE 2.10

Particulate Sulfur to Total Sulfur Ratio
Mean Value for the Years 1972 through 1974
Grouped by Monitoring Agency and Location

Region	Monitoring Site (Mean Value of f_s)					
	NASN		CHESS		LAAPCD	
Los Angeles County Central					Lynwood*	0.10
	Los Angeles	0.36			Los Angeles	0.15
	Pasadena	0.39			Pasadena	0.14
	Glendale	0.39				
Orange County			Garden Grove	0.39		
	Anaheim	0.39	Anaheim	0.50		
	Santa Ana	0.42				
Eastern San Gabriel Valley			West Covina	0.35	Azusa	0.15
			Glendora	0.40		
Los Angeles County Coastal			Santa Monica	0.43	West L.A.	0.15
					Lennox	0.13
	Torrance	0.48				
	Long Beach	0.28				
Inland-West					Reseda	0.20
			Thousand Oaks	0.53		
Inland-East	San Bernardino	0.59				
Adjacent Air Basin			Vista	0.60		

*1974 only

between time of collection and later analysis (see Appendix B1). CHESS and NASN values of f_s should be considered as upper bounds to the true value of f_s.

Because of the likelihood that all available SO_2 data sets are systematically biased to an unknown degree, no attempt will be made to place confidence intervals on the f_s data through ordinary statistical techniques. Instead, a limited amount of statistical information on each data set will be given in Table 2.11 for the entire three year period, and in Tables 2.12, 2.13, and 2.14 for the individual years 1972, 1973 and 1974, respectively. Then qualitative conclusions will be drawn from the temporal and spatial gradients in f_s values apparent from within groups of stations using the same monitoring methods.

In Figure 2.21, average values of f_s at the NASN and CHESS stations during the years 1972 through 1974 are shown in relation to monitoring site location. At Long Beach near major coastal point sources in the Los Angeles Harbor area, the three year average value of f_s is seen to be in the range of 0.20 to 0.30. Intermediate locations in the center of the Los Angeles Basin, like Glendale, Los Angeles, and Pasadena, show values of f_s which are higher, in the range of 0.30 to 0.40. Further downwind at Glendora, f_s increases to above 0.40. By the time that air masses reach inland locations as distant as San Bernardino most of the sulfur is in the particulate phase. Our expectation that f_s should increase with distance downwind from major SO_2 sources in the harbor area seems supported. Values of f_s at Vista, Thousand Oaks, Santa Monica and central Orange County are more difficult to interpret

TABLE 2.11

Particulate Sulfur to Total Sulfur Ratio, f_s
for the Period 1972 through 1974

		SAMPLE ARITHMETIC MEAN VALUE OF f_s	SAMPLE ARITHMETIC STANDARD DEVIATION	NUMBER OF SAMPLES
LOS ANGELES	LAAPCD	0.15	0.10	209.00
AZUSA	LAAPCD	0.15	0.11	210.00
WEST LA	LAAPCD	0.15	0.10	214.00
RESEDA	LAAPCD	0.20	0.15	214.00
LENNOX	LAAPCD	0.13	0.08	217.00
PASADENA	LAAPCD	0.14	0.11	213.00
LYNWOOD	LAAPCD	0.10(b)	0.07(b)	68.00(b)
VISTA	CHESS	0.60	0.30	954.00
SANTA MONICA	CHESS	0.43	0.28	756.00
THOUSAND OAKS	CHESS	0.53	0.32	780.00
ANAHEIM	CHESS	0.50	0.31	841.00
GARDEN GROVE	CHESS	0.39	0.29	812.00
GLENDORA	CHESS	0.41	0.25	833.00
WEST COVINA	CHESS	0.35	0.24	772.00
TORRANCE	NASN	0.48	0.25	65.00
LONG BEACH	NASN	0.28	0.19	61.00
LOS ANGELES	NASN	0.36	0.22	60.00
BURBANK	NASN	(a)	(a)	0.0
GLENDALE	NASN	0.39	0.24	53.00
PASADENA	NASN	0.39	0.19	61.00
ANAHEIM	NASN	0.39	0.21	78.00
SANTA ANA	NASN	0.42	0.21	72.00
ONTARIO	NASN	(a)	(a)	0.0
RIVERSIDE	NASN	(a)	(a)	0.0
SAN BERNARDINO	NASN	0.59	0.26	62.00

Notes: (a) Data unavailable.

(b) 1974 only.

TABLE 2.12

Particulate Sulfur to Total Sulfur Ratio, f_s
for the Year 1972

		SAMPLE ARITHMETIC MEAN VALUE OF f_s	SAMPLE ARITHMETIC STANDARD DEVIATION	NUMBER OF SAMPLES
LOS ANGELES	LAAPCD	0.15	0.08	66.00
AZUSA	LAAPCD	0.16	0.10	67.00
WEST LA	LAAPCD	0.17	0.09	71.00
RESEDA	LAAPCD	0.22	0.13	72.00
LENNOX	LAAPCD	0.13	0.07	73.00
PASADENA	LAAPCD	0.16	0.10	70.00
LYNWOOD	LAAPCD	(a)	(a)	0.0
VISTA	CHESS	0.60	0.26	304.00
SANTA MONICA	CHESS	0.44	0.25	215.00
THOUSAND OAKS	CHESS	0.53	0.25	196.00
ANAHEIM	CHESS	0.40	0.25	297.00
GARDEN GROVE	CHESS	0.37	0.26	214.00
GLENDORA	CHESS	0.36	0.19	274.00
WEST COVINA	CHESS	0.34	0.18	219.00
TORRANCE	NASN	0.42	0.22	22.00
LONG BEACH	NASN	0.31	0.22	21.00
LOS ANGELES	NASN	0.27	0.13	24.00
BURBANK	NASN	(a)	(a)	0.0
GLENDALE	NASN	0.34	0.20	23.00
PASADENA	NASN	0.38	0.18	21.00
ANAHEIM	NASN	0.37	0.17	27.00
SANTA ANA	NASN	0.47	0.19	27.00
ONTARIO	NASN	(a)	(a)	0.0
RIVERSIDE	NASN	(a)	(a)	0.0
SAN BERNARDINO	NASN	0.54	0.24	24.00

Note: (a) Data unavailable.

TABLE 2.13

Particulate Sulfur to Total Sulfur Ratio, f_s
for the Year 1973

		SAMPLE ARITHMETIC MEAN VALUE OF f_s	SAMPLE ARITHMETIC STANDARD DEVIATION	NUMBER OF SAMPLES
LOS ANGELES	LAAPCD	0.17	0.11	72.00
AZUSA	LAAPCD	0.14	0.11	72.00
WEST LA	LAAPCD	0.13	0.10	71.00
RESEDA	LAAPCD	0.21	0.18	72.00
LENNOX	LAAPCD	0.11	0.07	72.00
PASADENA	LAAPCD	0.16	0.12	72.00
LYNWOOD	LAAPCD	(a)	(a)	0.0
VISTA	CHESS	0.51	0.26	315.00
SANTA MONICA	CHESS	0.35	0.23	312.00
THOUSAND OAKS	CHESS	0.43	0.27	308.00
ANAHEIM	CHESS	0.68	0.30	314.00
GARDEN GROVE	CHESS	0.35	0.22	315.00
GLENDORA	CHESS	0.38	0.24	308.00
WEST COVINA	CHESS	0.29	0.19	304.00
TORRANCE	NASN	0.38	0.19	18.00
LONG BEACH	NASN	0.33	0.17	18.00
LOS ANGELES	NASN	0.35	0.15	18.00
BURBANK	NASN	(a)	(a)	0.0
GLENDALE	NASN	0.35	0.15	18.00
PASADENA	NASN	0.39	0.20	19.00
ANAHEIM	NASN	0.33	0.13	22.00
SANTA ANA	NASN	0.31	0.14	19.00
ONTARIO	NASN	(a)	(a)	0.0
RIVERSIDE	NASN	(a)	(a)	0.0
SAN BERNARDINO	NASN	0.52	0.20	17.00

Note: (a) Data unavailable.

TABLE 2.14

Particulate Sulfur to Total Sulfur Ratio, f_s for the Year 1974

		SAMPLE ARITHMETIC MEAN VALUE OF f_s	SAMPLE ARITHMETIC STANDARD DEVIATION	NUMBER OF SAMPLES
LOS ANGELES	LAAPCD	0.15	0.11	71.00
AZUSA	LAAPCD	0.14	0.12	71.00
WEST LA	LAAPCD	0.14	0.11	72.00
RESEDA	LAAPCD	0.18	0.14	70.00
LENNOX	LAAPCD	0.13	0.09	72.00
PASADENA	LAAPCD	0.11	0.09	71.00
LYNWOOD	LAAPCD	0.10	0.07	68.00
VISTA	CHESS	0.68	0.33	335.00
SANTA MONICA	CHESS	0.55	0.34	229.00
THOUSAND OAKS	CHESS	0.65	0.36	276.00
ANAHEIM	CHESS	0.40	0.30	230.00
GARDEN GROVE	CHESS	0.46	0.35	283.00
GLENDORA	CHESS	0.49	0.31	251.00
WEST COVINA	CHESS	0.45	0.31	249.00
TORRANCE	NASN	0.60	0.27	25.00
LONG BEACH	NASN	0.21	0.17	22.00
LOS ANGELES	NASN	0.48	0.32	18.00
BURBANK	NASN	(a)	(a)	0.0
GLENDALE	NASN	0.52	0.35	12.00
PASADENA	NASN	0.41	0.19	21.00
ANAHEIM	NASN	0.45	0.27	29.00
SANTA ANA	NASN	0.44	0.24	26.00
ONTARIO	NASN	(a)	(a)	0.0
RIVERSIDE	NASN	(a)	(a)	0.0
SAN BERNARDINO	NASN	0.72	0.28	21.00

Note: (a) Data unavailable.

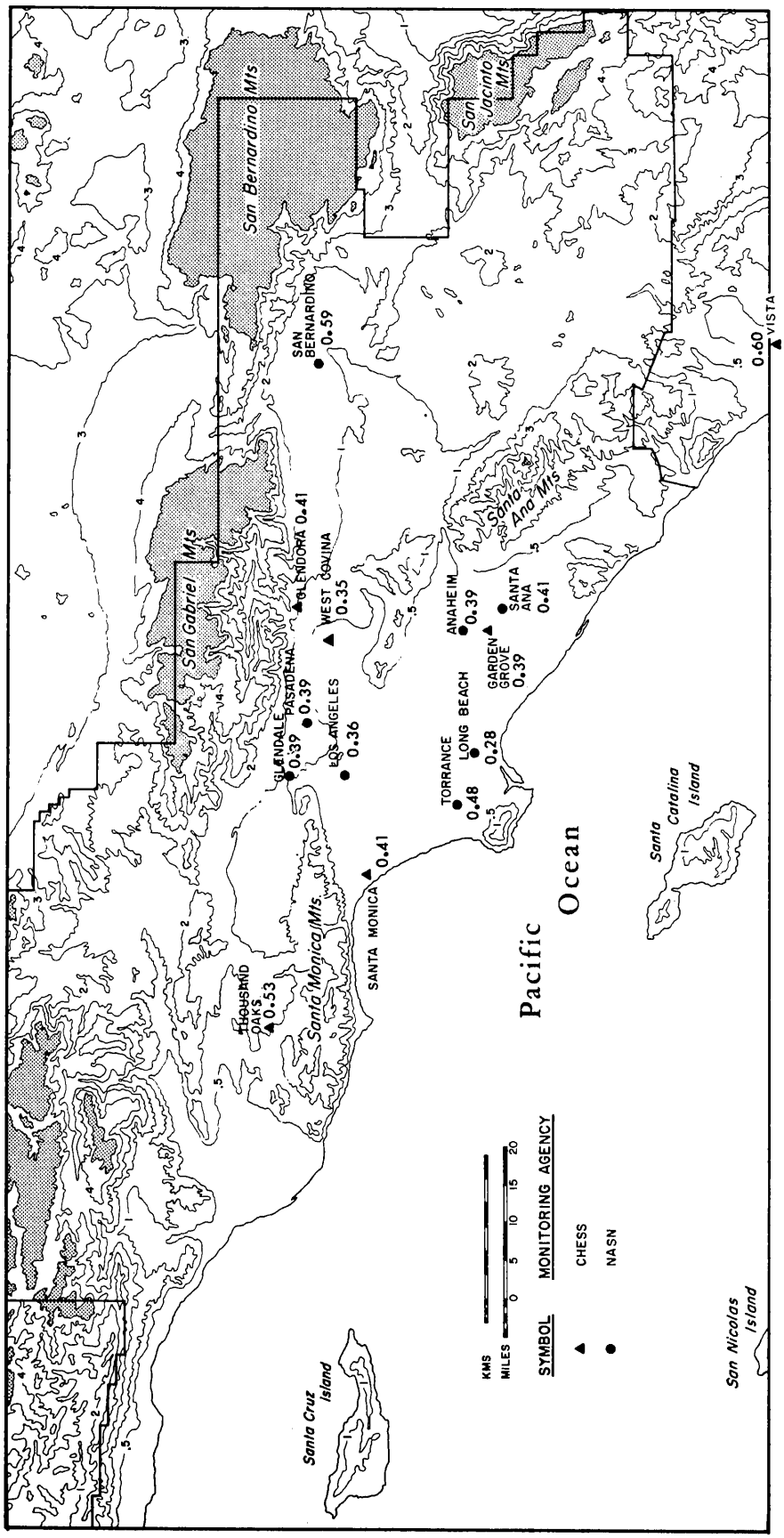

FIGURE 2.21

Average Values of f_s During the Years 1972 through 1974 at CHESS and NASN Monitoring Stations

because those locations lie to the side of the predominant direction of transport of sulfur oxides from Los Angeles harbor area emission sources. The Torrance station appears to be "upwind" of the harbor industrial complex. Comparable values of f_s in the San Fernando Valley are unavailable, but the LAAPCD data indicate that f_s at Reseda is high in relation to downtown Los Angeles.

Appendix B7 displays the seasonal trends in f_s values computed from data of the CHESS and LAAPCD networks. Also shown is the seasonal trend in a second statistic, $\overline{f_s}$, which is the ratio of *monthly average* particulate sulfur oxides concentration to *monthly average* total sulfur oxides concentration. This second statistic is more readily computed from the results of a long-term average air quality model than is the average value of f_s itself. It therefore will become convenient to compare air quality model results to trends in $\overline{f_s}$ as one means of assessing air quality model performance.

While sulfate concentration trends were found to be very similar over widespread areas of the South Coast Air Basin, there are some distinct, and often puzzling differences between f_s observations at nearby monitoring stations. The most obvious differences are still between monitoring networks using different measurement techniques. The LAAPCD and CHESS networks both show relative peaks in f_s during the summer months, but as with the annual averages, the LAAPCD f_s values are consistently roughly half the magnitude of those obtained by CHESS. Even internally to the CHESS program, there are some noteworthy differences between results at nearby monitoring stations. At the start of

1973, CHESS f_s measurements at Anaheim begin to climb sharply above those calculated at the Garden Grove station located less than two miles away. Then during 1974, some uncharacteristically high f_s values are apparent periodically at a larger number of CHESS monitoring sites. One is led to speculate that the CHESS network may have encountered sample collection problems at about the same time that they changed the volume of West-Gaeke reagent in their bubblers and reduced sampler air flow rate in order to match the Federal reference sampling method for SO_2 employed by NASN (see Appendix B1).

In summary, data on the fraction of atmospheric sulfur present as sulfates are not as reliable as one would like. These problems arise from difficulties in measurement of very low sulfur dioxide levels by the methods used at the stations under study. In spite of these problems, relative spatial variations in three year average f_s values from CHESS and NASN stations using similar SO_2 measurement procedures are consistent with our prior expectations. The lowest values of f_s are found near major SO_2 source areas, and f_s values increase with distance downwind as SO_2 is removed at the ground or is oxidized in the atmosphere to form sulfates. Actual use of numerical values of f_s in our modeling study should proceed with caution. About all that can be said is that model results should fall at or below the long-term average f_s values reported by CHESS and NASN stations, but above values calculated from LAAPCD data.

2.4 Atmospheric Oxidation of SO_2 to Form Sulfates

The observed uniformity of average sulfate levels is in marked contrast to the highly localized nature of the major sources of precursor sulfur dioxide. For a conserved or slowly decaying pollutant emitted from coastal point sources, one expects pollutant concentration to drop greatly with distance downwind as atmospheric dispersion and removal processes come into effect. Sulfur dioxide concentrations do decline, as expected, with distance inland from the coast. The contrasting constant sulfate levels with distance inland from major sulfur oxide sources is probably explained by a competition between dispersion which tends to lower pollutant concentrations and additional gas-to-particle conversion involving SO_2 which tends to build up sulfate concentrations. An additional possibility is that some sulfate formation occurs aloft or offshore during late night land breezes and early morning stagnation periods. This well-aged aerosol might then be swept across the Basin during the day by the advancing sea breeze, contributing roughly equal amounts of sulfate to successive air monitoring stations in passing. In either case, the rate at which SO_2 is oxidized to form sulfates will influence the magnitude of the sulfate concentrations observed.

2.4.1 An Overview of Atmospheric Sulfur Chemistry

The relative importance of various SO_2 to sulfate conversion mechanisms is poorly understood at present. SO_2 oxidation rates have been measured in the Los Angeles atmosphere and found to vary from one

percent to 15 percent per hour under photochemically active, daylight sea breeze conditions (Roberts, 1975). At least three general classes of chemical reactions could oxidize SO_2 at rates fast enough to account for observed sulfate levels. These possibilities include:

1. Homogeneous gas-phase oxidation of SO_2 by free radicals generated in Los Angeles photochemical smog.
2. Heterogeneous phase processes involving absorption of SO_2 by aqueous particles in the atmosphere followed by oxidation in the liquid phase.
3. Heterogeneous phase processes involving surface adsorption of SO_2 by carbonaceous or metal oxide particles, followed by oxidation to sulfate.

The scientific literature supporting specific chemical reaction mechanisms within these three broad classes is voluminous. A number of review articles have been written which taken together provide a good summary of current knowledge (Urone and Schroeder, 1969; Bufalini, 1971; Calvert, 1973; Harrison, Larson and Hobbs, 1975; Sander and Seinfeld, 1976).

Homogeneous gas phase reactions considered to be important in explaining atmospheric sulfur dioxide oxidation include:

1. oxidation of SO_2 by hydroxyl (OH) radicals

$$SO_2 + OH + M \rightarrow HSO_3 + M \qquad (2.2)$$

2. oxidation of SO_2 by HO_2 radicals

$$HO_2 + SO_2 \rightarrow SO_3 + OH \quad (2.3a)$$

$$HO_2 + SO_2 \rightarrow SO_2HO_2 \quad (2.3b)$$

3. oxidation of SO_2 by other oxy-, peroxy-, and ozonide free radicals such as RO, RO_2, $RCO(O_2)$ (for example the ozone-olefin - SO_2 reactions studied by Cox and Penkett, 1972; and McNelis, 1974).

$$SO_2 + RO \rightarrow ROSO_2 \quad (2.4)$$

$$SO_2 + RO_2 \rightarrow SO_3 + RO \quad (2.5a)$$

$$SO_2 + RO_2 \rightarrow SO_2RO_2 \quad (2.5b)$$

$$SO_2 + RCO(O_2) \rightarrow RCO_2 + SO_3 \quad (2.6)$$

Rate constants for this latter group of reactions involving organic free radicals are poorly established at present, but they are thought to be fast enough to be important in a heavily polluted atmosphere.

Sander and Seinfeld (1976) embedded the first two of these SO_2 free radical reactions (i.e. OH and HO_2 reactions) within a basic hydrocarbon/NO_x mechanism suitable for simulating smog photochemistry. They then tested the speed of that homogeneous reaction system against SO_2 oxidation rates observed in a wide variety of laboratory experiments. They conclude for a purely homogeneous system "...that known reactions involving SO_2 for which rate constants have been measured are insufficient in themselves to account for observed SO_2 oxidation rates

in NO_x/hydrocarbon/SO_2 systems." They speculate that reactions for which rate constants are currently unknown (e.g. organic peroxy radical reactions) may be important or that heterogeneous processes are responsible for accelerated SO_2 oxidation even in experimental systems in which heterogeneous processes were avoided to the greatest extent possible.

In a further simulation roughly approximating atmospheric photochemistry in Los Angeles, Sander and Seinfeld (1976) estimated a *maximum* SO_2 oxidation rate of 4.5% per hour due to purely homogeneous processes. That simulation included reactions and rate estimates for SO_2 oxidation by OH, HO_2, RO_2, RCO_3, and $O(^3P)$ radicals. Oxidation of SO_2 by OH and HO_2 radicals still dominated, and the maximum rate of sulfate formation was still slower than some of the atmospherically observed rates of SO_2 oxidation reported for Los Angeles by Roberts (1975).

Heterogeneous chemical reactions involving gaseous/liquid phase interactions have long been suspected as important routes for promoting SO_2 oxidation to form sulfates. Health related studies continually point out that increased mortality associated with SO_x and particulate air pollution observed in the Muse Valley, Belgium (1930), Donora, Pennsylvania (1948), and London, England (1952) were all accompanied by fog. The supposition is that large amounts of acid aerosol may have been formed by fixation of sulfur oxides inside aqueous droplets. Data needed to prove or refute that conjecture are unavailable for those particular pollution episodes. But a large number of field and

laboratory experimental studies show that the following types of heterogeneous SO_2 oxidation processes involving aqueous particles can occur at a rapid enough rate to be important in the atmosphere:

1. Oxidation of SO_2 by O_2 in well buffered droplets (Scott and Hobbs, 1967). The overall reaction including gas transfer to the droplet is

$$2SO_2 + 2H_2O + O_2 \rightarrow 2H_2SO_4 \tag{2.9}$$

2. Metal-ion catalyzed oxidation of SO_2 by O_2 in the liquid phase (Johnstone and Coughanowr, 1958; Junge and Ryan, 1958; Foster, 1968, and many others). The overall reaction including gas transfer to the droplet is

$$2SO_2 + 2H_2O + O_2 \xrightarrow{\text{catalyst}} 2H_2SO_4 \tag{2.10}$$

3. Oxidation of SO_2 by photochemical oxidants dissolved in droplets (Penkett, 1972). One example of this class of reactions (including gaseous transfer to the droplet) presumably is

$$SO_2 + H_2O + O_3 \rightarrow H_2SO_4 + O_2 \tag{2.11}$$

These liquid phase reactions are substantially affected by droplet acidity. As acid concentrations build up in a droplet, oxidation of dissolved SO_2 can slow to a negligible rate. But for clean clouds at a pH of about 5.6 these mechanisms proceed to oxidize SO_2 to form sulfate at a rate of from several percent per hour to over ten percent per hour. At high catalyst concentrations or high oxidant concentrations, reaction types (2.10) and (2.11) above are still significant

even for moderately acidic aerosols at pH 4.6 (ref. Harrison, Larson and Hobbs, 1975). Catalyst type would also be an important factor, with transition metal ions of manganese and vanadium noted for their promotion of rapid oxidation, and iron often considered to be an important catalyst because of its relative abundance.

High SO_2 oxidation rates due to these heterogeneous reactions are often associated with high ambient relative humidity for two reasons. First, as relative humidity increases, hygroscopic particles pick up liquid water and grow in size, providing an aqueous medium in which the reactions can take place. Secondly, as humidity increases further, additional condensation of water can dilute aerosol acidity and cause the reaction rate internal to the droplet to increase above what it would have been otherwise.

Heterogeneous phase reactions involving SO_2 adsorption on the surfaces of carbonaceous or metal oxide particles are not as well understood at present, but possibly are important. An investigation of SO_2 reactions on the surfaces of soot particles by Novakov, et al. (1974) showed rapid conversion to sulfate. The rate of reaction in that mechanism was also thought to increase sharply with increasing relative humidity.

2.4.2 An Empirical Investigation of Factors Affecting Sulfur Oxides Chemistry and Dispersion in the Los Angeles Atmosphere

The variety of chemical reactions *potentially* leading to oxidation of SO_2 to form sulfates at a rate of several percent per hour is readily apparent. Several practical questions now arise. Is any

single type of well-known reaction responsible for the bulk of the high sulfate episodes observed in Los Angeles? Is that reaction path simple enough to simulate from first principles in an air quality model which will be run for long periods of time, or must some approximations be made?

An empirical analysis of downtown Los Angeles air monitoring data was conducted by Cass(1975) to see if day-to-day fluctuations in sulfate level at downtown Los Angeles could be shown to depend on fluctuations in meteorological dispersion or on factors affecting SO_2 to sulfate conversion rates. Meteorological dispersion indicators studied include early morning and afternoon inversion heights plus daily average wind speed, solar radiation intensity, and temperature. While changes in gas-phase free radical reactions are unobservable from conventional air monitoring data, there are data on possible indicators of the intensity of daily photochemical smog activity, including oxidant concentrations, NO_2, and hydrocarbon level. Roberts (1975) showed that knowledge of ambient ozone levels improves the estimation of SO_2 oxidation rates in the Los Angeles atmosphere. If oxidation of SO_2 were occurring in the liquid phase on hydrated particles, then ambient relative humidity and suspended particulate concentrations would be important (along with such factors as ammonia concentration and catalytic metals levels, for which we do not have complete air monitoring data).

Data for over six hundred days of observation on air quality parameters and meteorological variables were reviewed, and 342 rainless

days with a complete set of observations on all variables of interest were located. A statistical description of the explanatory variables used is given in Appendix B8. This data set was matched to a step-wise regression model to determine which other atmospheric circumstances most closely track fluctuations in sulfate levels. Fluctuations in atmospheric variables generally have multiplicative effects on pollutant levels. For instance, halving the inversion height while doubling the reaction rate would quadruple expected sulfate concentrations, all other factors remaining equal. For this reason, the regression model was specified in multiplicative or log-linear form.

Results of these correlation studies are presented in Tables 2.15 and 2.16 for the entire data base of record and for those samples taken since the change in LAAPCD sampling schedule of September 1970. Sulfate concentrations appear to be strongly inversely proportional to changes in afternoon inversion height. Sulfate concentration is found to be strongly dependent on daily relative humidity (RH) levels. This dependence on relative humidity is consistent with the observation of numerous investigators that a variety of sulfate formation mechanisms accelerate at high humidity. Knowledge of total suspended particulate matter (TSP) concentration provides a significant improvement in model fit. This is interesting because the grouping $TSP \cdot (1-RH)^{-1}$ for a hygroscopic aerosol would provide a term very roughly proportional to

TABLE 2.15

Stepwise Regression of Log $SO_4^=$ on Logs of Other Pollutant and Meteorological Variables at Downtown Los Angeles (For Description of Data Base, See Appendix B8)
(from Cass, 1975)

RESULTS: 1965-1974 — 342 Days of Observation

First 8 Steps		Multiple Correlation Coefficient
STEP 1	$SO_4^= \propto \frac{1}{(\text{Inv Max})^{1.36}}$	0.60
STEP 2	$SO_4^= \propto \frac{1}{(1-RH)^{0.61}(\text{Inv Max})^{1.07}}$	0.65
STEP 3	$SO_4^= \propto \frac{(TSP)^{1.10}}{(1-RH)^{1.14}}$	0.66
STEP 4	$SO_4^= \propto \frac{(TSP)^{0.77}}{(1-RH)^{0.81}(\text{Inv Max})^{0.73}}$	0.70
STEP 5	$SO_4^= \propto \frac{(TSP)^{0.84}(\text{Inv Base})^{0.23}}{(\text{Inv Max})^{1.08}}$	0.71
STEP 6	$SO_4^= \propto \frac{(TSP)^{0.92}(\text{Inv Base})^{0.16}}{(1-RH)^{0.54}(\text{Inv Max})^{0.80}}$	0.73
STEP 7	$SO_4^= \propto \frac{(TSP)^{0.88}(\text{Inv Base})^{0.15}(\text{Avg O3})^{0.21}}{(1-RH)^{0.56}(\text{Inv Max})^{0.72}}$	0.74
STEP 8	$SO_4^= \propto \frac{(TSP)^{0.96}(\text{Inv Base})^{0.12}(\text{Avg O3})^{0.85}}{(1-RH)^{0.55}(\text{Inv Max})^{0.72}(\text{O3 Max})^{0.55}}$	0.75

VARIABLE TYPE	SYMBOL	ESTIMATED EXPONENT AT STEP 8	STANDARD ERROR OF THAT ESTIMATE
Total suspended particulate	TSP	0.95	0.11
$(1-\frac{\text{relative humidity}}{100})$	(1-RH)	-0.55	0.10
Afternoon inversion height	Inv Max	-0.72	0.10
Morning inversion base height	Inv Base	0.12	0.03
24 hour avg. oxidant	Avg. O3	0.85	0.18
Daily instantaneous oxidant peak	O3 Max	-0.55	0.15

TABLE 2.16

Stepwise Regression of Log $SO_4^=$ on Logs of Other Pollutant and Meteorological Variables at Downtown Los Angeles (For Description of Data Base, See Appendix B8)
(from Cass, 1975)

RESULTS: September 1970-1974 — 186 Days of Observation

First 5 Steps		Multiple Correlation Coefficient
STEP 1	$SO_4^= \propto \frac{1}{(1-RH)^{1.24}}$	0.66
STEP 2	$SO_4^= \propto \frac{(TSP)^{0.86}}{(1-RH)^{1.31}}$	0.78
STEP 3	$SO_4^= \propto \frac{(TSP)^{0.82}(Avg\ O3)^{0.44}}{(1-RH)^{1.28}}$	0.82
STEP 4	$SO_4^= \propto \frac{(TSP)^{0.65}(Avg\ O3)^{0.37}}{(1-RH)^{1.13}(Inv\ Max)^{0.39}}$	0.83
STEP 5	$SO_4^= \propto \frac{(TSP)^{0.75}(Inv\ Base)^{0.11}(Avg\ O3)^{0.39}}{(1-RH)^{0.92}(Inv\ Max)^{0.46}}$	0.85

VARIABLE TYPE	SYMBOL	ESTIMATED EXPONENT AT STEP 5	STANDARD ERROR OF THAT ESTIMATE
Total suspended particulate	TSP	0.75	0.09
$(1-\frac{\text{relative humidity \%}}{100})$	1-RH	-0.92	0.10
Afternoon inversion height	Inv Max	-0.46	0.10
Morning inversion base height	Inv Base	0.11	0.03
24 hour avg. oxidant	Avg. O3	0.39	0.07

the volume of aqueous solution available in the atmosphere at a given time.[2]

Further improvement in model fit is provided by the inclusion of daily average oxidant concentration.

Beyond this point, improvements in model fit are provided mainly by attempts to better estimate the effects of the above phenomena through inclusion of oxidant peak data, for example, rather than by entry of new explanatory variables. The unexpected inclusion of morning inversion base in the numerator of these regression expressions indicates that very low morning inversion base heights are associated with low sulfate levels. That finding has since been confirmed by APCD analysts (Zeldin, Davidson, Brunelle and Dickenson, 1976), and by the California Air Resources Board (1976). The explanation seems to be that a relatively high morning inversion base (between 225 and 1100 meters above sea level) traps overnight emissions from elevated sources next to the ground within a thick moist marine layer, below an inversion which will be difficult to burn off during the next day. A very high sulfate day often has a 600 meter morning inversion base height with little or no rise in inversion base during the day, yielding a lower than average afternoon maximum mixing depth. Relatively little vertical

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[2] Neiburger and Wurtele's (1949) discussion of water uptake by hygroscopic atmospheric particles develops the approximation that particle radius is roughly proportional to [particle solute mass/(1-RH)]$^{1/3}$. Particle volume is thus proportional to solute mass times (1-RH)$^{-1}$. If TSP is proportional to soluble particulate matter and the relative size distribution of dry solute mass per particle is preserved from day to day, then the above approximation follows.

dilution of pollutants is achieved. In the absence of much vertical inversion base movement, little down-mixing of dry air from aloft will occur, and relative humidity stays high throughout the day. In contrast, surface-based inversions overnight isolate the effluent from elevated emission sources well above ground level receptors for many hours. These overnight surface inversions often are rather weak, and may burn off completely by the following afternoon[3]. Separation of elevated emissions from ground level receptors at night, followed by high dilution of pollutants the next afternoon may explain why days with very low morning inversion base heights have less than average potential for creating high sulfate concentrations.

It is significant that changes in *scalar* average wind speed seem to bear little relation to sulfate concentrations. For primary pollutants linked to ground level area source emissions, such as total hydrocarbons or CO, scalar wind speed determines initial atmospheric dilution. When nearby sources dominate air quality for these pollutants, then scalar wind speed and measured pollutant concentration are significantly negatively correlated. For a secondary pollutant formed in the atmosphere, such as sulfate, extensive mixing occurs during pollutant formation. Initial dilution is thus less important to

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[3]A spot survey of morning and afternoon inversion base data given by the Los Angeles Air Pollution Control District (1972, 1973) indicates that about 60% of the mornings with surface inversions are followed by afternoons with higher than usual (1219+ m; 4000+ ft) maximum mixing depths over downtown Los Angeles. Most of these days had afternoon mixing depths greater than the APCD's maximum recorded level of 1524 m (5000 ft).

observed concentrations than is the volume of the reactor (inversion height), the speed of the reaction, and total retention time in the airshed (which depends on vector-valued wind behavior).

A second approach to understanding the circumstances associated with high sulfate levels in Los Angeles is more subjective, but perhaps as instructive. Due to the typical time lag of several months between sulfate sample collection and analysis, few accounts of sulfate air quality contain any mention of the observer's description of the way the weather "looked" on days of abnormally high sulfate values. Of particular interest is whether weather conditions were conducive to high photochemical smog levels which might imply a gas-phase SO_2 to sulfate conversion mechanism, or whether conditions were typical of a London fog-type situation in which liquid-phase oxidation of SO_2 predominates. The LAAPCD sulfate data base was scanned to select all days of record through the end of 1974 for which 24-hour average sulfate levels exceeded 30 $\mu gm/m^3$ at downtown Los Angeles.[4] Sixty-two such days were found. The weather <u>forecast</u> printed for each day in the <u>Los Angeles Times</u> was then reviewed, and the question asked, "Was the word fog mentioned in the forecast for that day at locations within Los Angeles and Orange Counties?" Then the U.S. Weather Service data logs for each of these days at coastal airports were reviewed to see if fog was <u>observed</u> that day at those locations. Unfortunately, Weather Service fog observations are

[4] If duplicate samples were available, they were averaged to obtain the daily values used.

unavailable at downtown Los Angeles. Then, daily oxidant concentrations at downtown Los Angeles were recorded for both the daily instantaneous peak and 24-hour average corresponding to the period of each sulfate sample. The results of this sulfate episode survey are shown in Table 2.17 (from Cass, 1975).

Review of Table 2.17 shows that fog was forecast at some point in the Basin on all but 10 days of the 62 days of high sulfate values. Four of these remaining days contained forecasts for "drizzles" or "sprinkles", leaving only 6 days of high sulfate without a prior indication of high moisture concentrations. Of those 6 days, fog was observed on 3 days, even though not forecast; drizzle occurred on a fourth day, and a fifth day showed the highest average relative humidity of the entire 62-day sample population. On 29 days, fog was forecast for the immediate vicinity of the air monitoring station at downtown Los Angeles. Fog was observed at coastal airports near major SO_2 sources on 31 of the days in question, and other indicators of condensation such as trace precipitation or drizzles were observed on 10 additional days. In most cases the weather forecasts were for "late night and early morning low clouds and fog". While this is not a particularly uncommon forecast, high sulfate values are likewise common in the Los Angeles area. Oxidant levels on these days are quite variable: 9 days with instantaneous maximum over 0.20 ppm; 28 days between 0.20 and 0.10 ppm instantaneous maximum; 22 days when ozone levels never exceeded 0.10 ppm at any time at downtown Los Angeles. While higher oxidant concentrations in this air basin usually

TABLE 2.17

Atmospheric Humidification and Ozone on Days With

30 $\mu gm/m^3$ $SO_4^=$ or Greater at Downtown Los Angeles

DATE			DOWNTOWN LOS ANGELES SULFATE	WAS FOG MENTIONED IN WEATHER FORECAST?					WAS FOG OBSERVED?		APPROXIMATE 24 HOUR AVG RELATIVE	OZONE	
Month	Day(s)	Year	($\mu gm/m^3$)	L. A.	Beaches	San Fernando Valley	San Gabriel Valley	Orange County	L. A. Airport	Long Beach Airport	HUMIDITY @LA	24hr Avg (pphm)	Inst Max (pphm)
8	19/20	65	34.0					b			90.0	4.6	15
3	28/29	66	33.2	"drizzles"	"drizzles"	"drizzles"	"drizzles"	b			b	4.5	12
9	27/28	67	30.6			Yes	Yes	Yes	T. Precip	b	81.5	3.5	15
10	10/11	67	33.5	Yes	Yes	Yes	Yes	Yes	Yes 2	Yes 2ce	72.4	5.8	24
10	25/26	67	34.6	Yes	Yes	Yes	Yes	Yes	Yes	Yes 2e	75.9	6.4	29
2	20/21	68	34.4	Yes	Yes	Yes	Yes	Yes	b	Yes g	85.0	1.6	5
7	17/18	68	47.2						Yes d	Yes f	81.7	6.8	22
1	8/9	69	39.4	Yes	Yes	Yes	Yes	Yes			77.7	1.5	3
3	19/20	69	43.2	Yes	Yes	Yes	Yes	Yes	b	b	60.3	3.9	17
5	21/22	69	45.7	Yes		Yes	Yes	Yes	T. Precip c		77.3	5.1	12
7	9/10	69	31.2			Yes	Yes	Yes	Yes		70.0	4.6	14
8	27/28	69	43.6			Yes	Yes	Yes	Yes e		77.9	7.0	21
9	24/25	69	41.6	Yes		Yes	Yes	Yes			78.5	b	b
1	21/22	70	44.5	Yes					Yes 2	Yes 2	89.6	1.3	3
3	25/26	70	30.4	Yes	Yes	Yes	Yes	Yes	T. Precip c		67.1	4.0	13
6	3/4	70	42.8	Yes	Yes	Yes a	Yes a	Yes	Yes e	Yes e	63.5	3.8	17
7	8/9	70	34.3								76.3	3.7	14
8	5/6	70	30.1	Yes		Yes	Yes	Yes	Yes c	Yes 2c	72.2	4.0	13
8	10/11	70	43.8	Yes				Yes	Yes 2	Yes 2e	64.2	4.8	17
9	2	70	33.0	Yes	Yes			Yes			75.7	6.0	21
10	5	70	38.6	Yes	Yes	Yes	Yes	Yes	T. Precip	T. Precip f	87.2	2.3	6
10	19	70	39.3	Yes	Yes						78.8	3.1	12
1	25	71	54.2	Yes		Yes	Yes	Yes	Yes	Yes	65.8	2.8	9
2	1	71	30.1		Yes			Yes		Yes 2	69.6	1.2	2
2	8	71	41.1	Yes	Yes	Yes	Yes	Yes	Yes	Yes 2	69.1	2.0	10
2	15	71	30.7	Yes		Yes	Yes	Yes	Yes e		71.9	1.8	5
3	22	71	39.2				Yes				71.0	b	b
3	24	71	51.7			"drizzle"	"drizzle"				73.3	1.9	6
5	12	71	39.0			Yes	Yes	Yes	Yes	Yes	84.5	1.9	9
7	7	71	43.2			Yes	Yes				72.4	3.8	13
7	22	71	47.9			"sprinkles"	"sprinkles"		T. Precip		76.1	3.6	12
8	21	71	31.1				Yes				70.0	3.7	12
9	15	71	32.6	Yes	Yes	Yes	Yes	Yes			67.9	1.1	4
11	9	71	39.7	Yes	Yes	Yes	Yes	Yes	Yes 2	Yes 2	66.9	3.2	9
1	8	72	34.5	Yes	Yes			Yes	Yes	Yes	79.6	1.1	3
1	18	72	38.5	Yes	Yes	Yes	Yes	Yes	Yes	Yes	82.3	1.2	3
1	23	72	41.8	Yes			Yes	Yes		Yes	83.0	1.3	4
2	17	72	35.2	Yes	Yes			Yes	Yes 2	Yes 2	73.5	2.0	7
3	8	72	32.9	"drizzles"	Yes	Yes	Yes	"drizzles"			84.5	2.6	7
3	13	72	55.5	Yes	"drizzles"	Yes	Yes	Yes	Yes		87.7	2.2	9
3	18	72	52.6	"drizzles"		"drizzle"	Yes	"drizzle"	Yes f		83.7	4.2	13
6	1	72	33.3						Yes f		80.0	5.5	21
8	5	72	34.4			Yes	Yes				60.9	4.2	13
4	12	73	37.5		Yes	Yes	Yes	Yes			78.1	3.6	12
4	27	73	50.3						Yes	Yes	78.6	2.0	8
5	12	73	42.0	Yes	Yes	Yes	Yes	Yes	"drizzle"	"drizzle"	80.0	3.4	8
5	17	73	72.0		Yes	Yes	Yes	Yes	Yes	"drizzle"	75.6	3.5	13
6	26	73	52.0	Yes	Yes	Yes	Yes	Yes	Yes	Yes	68.6	4.6	24
7	1	73	42.2				Yes				74.5	4.3	14
7	6	73	35.7			Yes	Yes			T. Precip	80.8	1.8	6
7	11	73	42.6			Yes	Yes				75.8	3.7	13
7	31	73	31.1			Yes	Yes		Yes f		75.9	3.7	12
8	5	73	30.6						T. Precip	T. Precip	85.3	4.1	10
9	14	73	42.8	"drizzle"	"drizzle"	"drizzle"	"drizzle"	"drizzle"		"drizzle"	86.8	4.2	11
9	19	73	36.1			Yes	Yes				83.5	4.4	19
11	8	73	39.0		Yes			Yes	Yes	Yes 2	64.5	2.3	8
5	7	74	33.8			Yes	Yes				84.3	5.3	11
6	6	74	42.3		Yes	Yes	Yes	Yes	T. Precip		78.1	3.9	12
6	11	74	44.5			Yes	Yes	Yes			78.9	4.8	11
9	10	74	32.4		Yes	Yes	Yes	Yes	Yes	Yes	76.9	6.7	24
9	19	74	38.9	Yes	Yes	Yes	Yes	Yes	Yes		78.8	4.8	21
10	14	74	38.4	Yes	Yes	Yes	Yes	Yes	Yes 2	Yes 2	75.1	4.9	18

Notes:

a Fog forecast for early part of second day on 8:00 am to 8:00 am sampling schedule
b Data not immediately available
c Observed during early part of second day on 8:00 am to 8:00 am sampling schedule
d Fog observed during second day segment of sample - no time of observation given
e Observed in hours prior to beginning of sample
f No time indicated for observation (possible internal inconsistency in records)
g Fog prior to sample, trace precipitation or "drizzle" during sample
2 Heavy Fog

Relative humidity and ozone averages are taken for the 24 hour period corresponding to sulfate samples. Missing hourly data were replaced by linear interpolation between adjacent data points prior to averaging. 24 hour average relative humidity values are approximate since observations are taken for 14 hours daily, thus necessitating extensive interpolation.

T. Precip. - Trace of precipitation

(Source: Cass, 1975)

occur inland from downtown Los Angeles, it must be remembered that the sulfate measurements studied here were taken at downtown Los Angeles and oxidant concentrations measured farther downwind may not be particularly relevant to explaining events at this location.

From the above discussion we wish to draw two more important physical generalizations.

Generalization 6: The most important phenomena explaining the large fluctuations in sulfate level from day to day are meteorological in nature. Low afternoon inversions concentrate sulfate pollutants near ground level. High relative humidity or fog seems to accelerate the conversion of SO_2 to form sulfate or to otherwise increase the total quantity of sulfate formed.

Generalization 7: A variety of sulfate formation mechanisms are probably important in the Los Angeles atmosphere.

From the order of entry of explanatory variables in the regression results of Tables 2.15 and 2.16, plus the persistence of fog associated with high sulfate levels in Table 2.17, one is led to speculate that heterogeneous reactions involving wetted particles are the dominant determinants of SO_2 oxidation rate on days of high sulfate levels in the Los Angeles Basin. However, apparent dependence of sulfate levels on both relative humidity, photochemical indicators (oxidant) and ambient particulate concentrations suggest that sulfate levels do respond to increases in nearly all the main ingredients of all of the competitive reaction processes (while not responding significantly

to largely unrelated pollutants like total hydrocarbons, which are mostly a measure of the extent to which ambient methane has been diluted on a given day).

Rate constants and catalyst concentration data needed to model the details of the chemical conversion of SO_2 to form sulfate in an atmosphere characterized by a competition between these many possible reaction paths are simply unavailable. Some approximations must be made if modeling is to proceed on the basis of currently available data.

One reason why so many competitive reaction paths are under consideration is that all of these reactions are likely to result in a relatively slow macroscopically observed rate of SO_2 oxidation on the average over long periods of time. Overall average SO_2 oxidation rates of a few percent per hour are expected. A useful approach at this point would seem to be to concentrate on calculating this overall average oxidation rate from the available monitoring data.

Slow chemical conversion processes often are approximated well by a pseudo-first order (exponential) decay. In the absence of SO_2 deposition at the ground, the reaction of SO_2 to form sulfate would be simplified and expressed as:

$$\frac{dS_{SO_2}}{dt} = -k[S_{SO_2}] \tag{2.7}$$

where k is the pseudo-first order rate "constant" for oxidation of SO_2 by all competing chemical mechanisms acting simultaneously. Sulfur dioxide removal is accompanied by sulfate formation:

$$\frac{dS_{SO_4}}{dt} = k[S_{SO_2}] \qquad (2.8)$$

Data on atmospheric sulfate concentrations and bounds on the fraction of sulfur present in the particulate phase are available. That means that in an air quality modeling exercise one can assume successive values for k, and check those assumptions against a fully determined system until the value of k is attained that best satisfies both the observed sulfate levels and the required relationships between sulfate and SO_2. No arbitrary assumptions are required.

Simply knowing whether the average SO_2 conversion rate, k, is 3% per hour or 10% per hour would make a great deal of difference to the further work that a theoretical chemist might need to undertake to satisfactorily come up with a mix of mechanisms that would yield plausible results. Furthermore, knowledge of whether or not a strong seasonal variation in reaction rate was needed to explain summer sulfate peaks would help one generate a credible mix of reaction mechanisms.

2.5 Summary of Implications for a Sulfate Air Quality Modeling Study

The availability of sulfur dioxide and sulfate air quality data in the South Coast Air Basin has been reviewed. The years 1972 through 1974 appear to form an attractive base time period for a sulfate air quality modeling study. During those years, the Los Angeles APCD, EPA's CHESS program and the National Air Surveillance Network air monitoring programs operated concurrently, yielding the widest available geographic coverage of sulfate air quality data.

Spatial gradients in sulfate concentration during those base years suggest that the atmosphere over metropolitan Los Angeles is enriched in sulfates when compared to surrounding areas in all directions. Over the Channel Islands and the Mojave Desert, to the southwest and northeast of the Basin, respectively, sulfate concentrations averaged 3 to 5 $\mu gm/m^3$. Onshore, to the northwest of Los Angeles County at Thousand Oaks, and to the southeast in San Diego County at Vista, sulfate concentrations averaged about 9 $\mu gm/m^3$. In contrast, average sulfate concentrations in the center of the South Coast Air Basin within metropolitan Los Angeles, Orange, San Bernardino and Riverside Counties ranged from 11 to 14 $\mu gm/m^3$. This localized sulfate enrichment makes the central portion of the South Coast Air Basin an ideal candidate for a sulfur oxides emissions to sulfate air quality modeling study. A distinct increment in sulfate levels above background has been found in an area where long-distance transport from sources outside the air basin is unlikely to be the entire explanation for observed sulfate concentrations.

Seasonal fluctuations in sulfate air quality have been shown to be similar throughout the entire South Coast Air Basin. A broad summer seasonal peak is apparent in all years of record, with occasional high values occurring in some winters of record. Observations taken at most stations on the same day are so highly correlated that they would be considered mutually dependent. The implication for our modeling study is that the major factors influencing 24-hour average sulfate air quality are felt basin-wide. Detailed

spatial representations of meteorological parameters and chemical reactions within our air quality model may be unnecessary. A relatively uncomplicated emissions to air quality model should be attempted initially to test its explanatory power.

The fraction of atmospheric sulfur present as particulate sulfur oxides, f_s, has been explored in relation to major SO_x emission source locations and general air transport patterns in the South Coast Air Basin. Average values of f_s were found to vary widely from one monitoring organization to another, and even varied substantially between nearby stations within the same monitoring program. This is due to inconsistencies in measured sulfur dioxide levels from one station to another. Nevertheless, it was found that the fraction of total sulfur present as sulfates increases with distance downwind from major SO_2 emission sources located in the Los Angeles harbor area. This behavior is consistent with the hypothesis that SO_2 is converted to form sulfates in the atmosphere downwind of these emission sources. That behavior is also consistent with preferential removal of SO_2 at the earth's surface as air parcels move downwind. These two SO_2 removal processes will have to be considered in our modeling study. The available data on the fraction of sulfur present in the particulate phase was judged to be less reliable than the sulfate data, and will hamper attempts to accurately confirm the rate at which SO_2 is oxidized to form sulfates in the Los Angeles atmosphere.

The availability of monitoring data on both sulfates and fraction sulfur present as sulfates restricts the geographic area over which air

quality model calculations may be compared to field observations. The Los Angeles County and Orange County coastal plains, plus the San Gabriel Valley are relatively well monitored. In contrast, the San Fernando Valley contains only one sulfate monitoring site in its interior (Reseda) and one site at its entrance (Burbank). The same circumstance occurs in the San Bernardino Valley, where useful sulfate and sulfur dioxide data are available simultaneously only at a single isolated monitoring site. Sulfate data are unavailable in the Oxnard, Ventura and Santa Barbara portions of the airshed. The area over which a sulfur oxides emissions to sulfate air quality model might be specified with the possibility of closely verifying its predictions is largely confined to coastal Los Angeles County south of the Santa Monica Mountains, plus Orange County and the San Gabriel Valley.

Fluctuations in measured sulfate values from day-to-day have been shown to track changes in inversion height, relative humidity, total suspended particulate levels and oxidant concentrations. From these relationships, it is suggested that day-to-day fluctuations in sulfate concentration are driven mainly by changes in factors affecting SO_2 to sulfate reaction rate and by changes in the effective volume of the reactor.

Meteorological parameters important to sulfate dilution and transport are inversion height movement and vector valued wind. Very low morning inversions permit pollutant emissions from elevated sources to be injected at least temporarily above the mixed layer. Low afternoon inversions determine the maximum vertical dilution of air parcels

residing below the inversion base. Scalar valued wind speed did not prove significant in explaining changes in sulfate level from one day to the next. It is therefore suggested that vector valued wind behavior, which determines air parcel retention time in the air basin, would be more important to sulfate concentrations than initial dilution at the source.

Sulfate levels have been shown to closely track changes in relative humidity and suspended particulate levels, with additional intrusion of fog on days of very high sulfate concentrations. On this basis one could speculate that heterogeneous oxidation of SO_2 on or within wetted particles is very important to high sulfate levels in Los Angeles. Sulfate concentrations are also slightly (but significantly) higher on days with elevated oxidant levels. Thus a variety of homogeneous gas-phase sulfate formation mechanisms may also be important.

In light of the complexity of the details of the chemical reactions possible, chemical conversion of SO_2 to form sulfate will be modeled as a slow pseudo-first order reaction. Emphasis should be placed initially on solving for the overall SO_2 oxidation rate and on identifying any seasonal trend in oxidation rate that may guide future theoretical investigations.

Two central questions to be answered by a study of the long-term relationship between sulfur oxides emissions and sulfate air quality are posed. Can the demonstrated sulfate enrichment above background in the Los Angeles metropolitan area be reasonably explained in terms

of local sulfur oxides emission sources? And if so, how do sulfur oxides emissions which are concentrated at a relative handful of locations along the coast become mapped into an average sulfate air quality pattern which is so nearly uniform over such a large geographical area?